

2D Materials Focus Topic

Room 201B - Session 2D+EM+MI+NS+TF-MoM

2D Materials Growth and Fabrication

Moderator: Jing Xia, University of California Irvine

8:20am **2D+EM+MI+NS+TF-MoM-1 Wafer Scale Epitaxial Growth of Monolayer and Few-Layer WS₂ by Gas Source Chemical Vapor Deposition, Mikhail Chubarov, T Choudhury, J Redwing, The Pennsylvania State University**

Tungsten disulfide (WS₂) has been widely investigated due to its outstanding properties compared to other 2D TMD including a bandgap of 2 eV, relatively high theoretical electron mobility, valley spin polarization, among others. Commonly, the films are grown on amorphous substrates like SiO₂ and, consequently, consist of high angle grain boundaries after coalescence due to the random orientation of domains. These can act as scattering and recombination centers for charge carriers limiting device performance. To avoid this, a crystalline substrate and epitaxial growth is typically employed for general thin film deposition although this approach has not been extensively investigated for 2D TMD monolayers. Large area growth is also crucial to show technological feasibility of the material for wafer-scale device fabrication.

In this work, we employ cold wall gas source chemical vapor deposition for the growth of WS₂ films on 2" (0001) α -Al₂O₃. To achieve coalesced monolayer growth over the entire substrate, we implemented a multi-step growth process modulating the metal precursor concentration during each of the steps. W(CO)₆ and H₂S were used as precursors in H₂ carrier gas. The deposition experiments were conducted over the temperature range from 750 °C to 1000 °C at a pressure of 50 Torr. Characterization of resulting samples was conducted using atomic force microscopy (AFM), in-plane X-ray diffraction (XRD) and room temperature Raman and photoluminescence (PL) measurements.

Initial studies showed that the WS₂ films exhibit multiple crystal orientations which evolve with growth temperature. At lower deposition temperature (750 °C), two orientations rotated 30° one from another were observed. At the high deposition temperature (1000 °C), five different crystal orientations were present. Among others, orientation with epitaxial relation of (10-10)WS₂//(10-10) α -Al₂O₃ was present at all temperatures. It was established that the unwanted orientations can be suppressed by increasing the H₂S concentration. Further adjustment of the growth and use of the multi-step growth process led to the formation of a coalesced epitaxial monolayer WS₂ on α -Al₂O₃ with XRD FWHM of 10-10 peak in ω being 0.09°. This value suggests well in-plane oriented domains with low edge dislocation density. A high intensity, narrow (FWHM=40 meV) PL peak positioned at 2.01 eV was observed for WS₂ films. Monolayer formation was confirmed from the AFM height profile (D =0.9 nm) and Raman measurements by observing spectral region where layer breathing and shear modes would appear. A fully coalesced, monolayer film was achieved using the multi-step growth process in a total time of 80 minutes.

8:40am **2D+EM+MI+NS+TF-MoM-2 Wafer Scale Deposition of Monolayer Transition Metal Dichalcogenides, Kortney Almeida, M Wurch, G Stecklein, L Bartels, University of California, Riverside**

Monolayer transition metal dichalcogenide (TMD) films are promising materials in the continuing development of nanoscale devices. Methods to produce wafer-scale monolayer TMD films have included tube-furnace chemical vapor deposition (CVD), liquid-phase exfoliation, and metal-organic CVD. These methods suffer from issues with particulate contamination, pyrophoric precursors, and high cost. Here we demonstrate the growth of homogeneous wafer-scale monolayer molybdenum disulfide (MoS₂) using solid inorganic and liquid organic precursors in a high-vacuum environment. These results are achieved using an amorphous SiO₂ substrate and without any powder or metal-organic precursors. Growth proceeds by the decomposition of carbon disulfide at a hot molybdenum filament, which yields volatile MoS_x precursors that precipitate onto a heated wafer. The continuous and homogeneous single-layer film of MoS₂ is deposited at wafer scale with a total growth time of fifty minutes. Various thicknesses of the thin films are also demonstrated by the manipulation of the filament power. Optical and electrical characterization indicates performance comparable to or better than MoS₂ film grown by other wafer-scale growth techniques. Our method provides a scalable process to deposit thin TMD films in a high vacuum environment.

9:00am **2D+EM+MI+NS+TF-MoM-3 Crystal Growth of 2D Materials: From Model Systems to Integrated Manufacturing, Stephan Hofmann, University of Cambridge, UK**

INVITED

In order to serve the industrial demand for "electronic-grade" 2D materials, we focus on chemical vapour deposition (CVD), and in this talk I will review our recent progress in scalable CVD [1] and device integration approaches of highly crystalline graphene, hexagonal boron nitride (h-BN) and transition metal dichalcogenide films. The systematic use of in-situ metrology, ranging from high-pressure XPS to environmental electron microscopy, allows us to reveal some of the key growth mechanisms for these 2D materials that dictate crystal phase, micro-structure, defects, and heterogeneous integration control at industrially relevant conditions [2,3]. I will focus on tailored CVD processes to achieve large monolayer h-BN domains with lateral sizes exceeding 0.5 mm. Importantly we show that depending on the process catalyst as-grown h-BN mono-layers can be easily and cleanly transferred using an entirely exfoliation-based approach.[4] We demonstrate sequential h-BN pick-up, opening a pathway to integrate CVD films in high quality 2D material heterostructures. Progress in growth reached a level where adequate characterisation of such 2D crystal layers over large areas has become a key challenge. Hence we also explore new non-contact characterisation methods [5,6]. We work on applications ranging from magnetic tunnel junctions [7] to sensing and single molecule analysis [8,9], and the talk will focus on some of the diverse yet connected integration challenges for CVD 2D films that present a key bottleneck towards reliable scale-up manufacturing and commercialisation.

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9:40am **2D+EM+MI+NS+TF-MoM-5 Understanding the Edge-Controlled Growth and Etching in Two-Dimensional Materials, Kai Xiao, X Li, X Sang, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; W Zhao, J Dong, Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan,44919, South Korea; A Puretzky, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; C Rouleau, Center for Functional Nanomaterials Brookhaven National Laboratory; F Ding, Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan,44919, South Korea; R Unocic, D Geohegan, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory**

Understanding the atomistic mechanisms governing the growth and etching of two-dimensional (2D) materials is of great importance in guiding the synthesis of large area, single-crystalline, high quality 2D crystals and heterostructures. In this talk, the growth-etching-regrowth process of monolayer 2D crystals by a CVD method will be discussed. We found that switching from growth to etching formed pores with various shapes in the single crystal domains which can be explained by edge-structure dependent growth process. In addition, combined with first principles theory, and ab initio simulations, in situ STEM imaging was used to understand the evolution of edge structure around pores in monolayers as a function of temperature and Mo chemical potential. Our results demonstrate that by varying the local chemical environment, we can trigger formation of 2D monolayer nanostructures terminated by different edge reconstructions during in situ heating and electron beam irradiation and form edge structures with metallic and/or magnetic properties. The ability to synthesize 2D nanostructures with metastable NW edges having predictable atomic structures opens the door to a wide range of novel 2D materials and heterostructures with electrical and magnetic properties as revealed by DFT, which could potentially act as functional building blocks for next-generation nano-devices.

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10:00am **2D+EM+MI+NS+TF-MoM-6 Synthesis and Characterization of 1T, 1T', and 2H MoTe₂ Thin Films, Thomas Empante**, University of California, Riverside; *Y Zhou*, Stanford University; *S Naghibi Alwillar*, El Camino College; *E Reed*, Stanford University; *L Bartels*, University of California, Riverside

Transition metal dichalcogenides (TMDs) have been of interest over the past few decades for their intriguing structural, electronic, and optoelectronic properties, particularly when scaled down to thin films. One of the most interesting TMD materials is molybdenum ditelluride (MoTe₂) because of its relative ease to attain multiple phases at room temperature, namely the metallic 1T' phase and the semiconducting 2H phase. Here we show a facile chemical vapor deposition process to synthesize not only the aforementioned phases but the elusive unreconstructed 1T phase by regulating the cooling rate and the addition of carbon dioxide during the reaction. Our experimental Raman spectroscopy results were compared to theoretical density functional theory calculations which verify the synthesis of all three phases. Electronic transport measurements were also used to characterize the films and show that the newly synthesized 1T phase is in good agreement with theoretical models depicting semi-metallicity as the material shows increased conductivity with elevated temperatures. In addition to the pure phase materials, mixed phase materials, such as 2H/1T, can be synthesized with slight alterations to the parameters leading to enhancements of the 2H phases' conductivity.

10:40am **2D+EM+MI+NS+TF-MoM-8 2D Anisotropic Semiconductors: Competing Phases by Alloys Engineering, Sefaattin Tongay**, Arizona State University **INVITED**

Akin to the enormous number of discoveries made through traditional semiconductor alloys, alloying selected 2D semiconductors enables engineering of their electronic structure for a wide range of new applications. 2D alloys have been demonstrated when two components crystallized in the same phase, and their bandgaps displayed predictable monotonic variation. By stabilizing previously unobserved compositions and phases of GaSe_{1-x}Te_x at nanoscales on GaAs(111), we demonstrate abnormal band bowing effects and phase instability region when components crystallize in different phases. Advanced microscopy and spectroscopy measurements show as tellurium is alloyed into GaSe, nanostructures undergo hexagonal to monoclinic and isotropic to anisotropic transition. There exists an instability region ($0.56 < x < 0.67$) where both phases compete and coexist, and two different bandgap values can be found at the same composition leading to anomalous band bowing effects. Findings also identify other potential systems including NbTiS₃ and shows the efficacy of the approach. Results highlight unique alloying effects, not existing in single-phase alloys, and phase engineering routes for potential applications in photonic and electronics.

11:20am **2D+EM+MI+NS+TF-MoM-10 Low-Defect, High-Uniformity Transfer-Free Graphene on SiO₂ by Thermal Chemical Vapor Deposition, Leslie Chan**, *D Tsai*, *Z Wang*, *C Carraro*, *R Maboudian*, University of California, Berkeley

Chemical vapor deposition (CVD) has emerged as the customary approach for scalable, controllable production of graphene for integrated devices. Standard CVD graphene must be transferred from a generic metal growth substrate onto the desired substrate (e.g., SiO₂), but this extra transfer often leads to wrinkles, contamination, and breakage that ultimately result in poor device performance. Several groups have demonstrated metal-catalyzed direct CVD-graphene growth on insulating substrates, but the final graphene products are deficient in quality and uniformity. This work details an expansion of the parameter space that enables lower-defect, higher-uniformity graphene than previously reported using nickel and copper catalysts, respectively. We introduce a mechanism based on carbon permeability that provides deeper insight into the growth process. Ultimately, these studies seek to inform the judicious choice of process parameters that will lead to large-area, high-quality, layer-controlled graphene directly on target substrates.

11:40am **2D+EM+MI+NS+TF-MoM-11 Barrier Based Approach to Modify Vapor Phase Concentrations for High Quality MoS₂ Growth, Dongzhi Chi**, *S Wong*, Institute of Materials Research and Engineering, Agency for Science Technology and Research, Singapore

Transition metal dichalcogenides, in particular, MoS₂, has attracted significant attention due to its unique electronic and physical properties. Much research efforts are directed towards achieving large area, high quality monolayer MoS₂ films. Using NiO foam as a reactive barrier, we achieved growth of highly homogeneous single layer MoS₂ on sapphire through chemical vapor deposition. As the NiO barrier reacts with MoO₃, the concentration of precursors reaching the substrate and thus nucleation density is effectively reduced. By doing so, single crystal MoS₂ grain sizes of up to 170 μm, together with continuous monolayers on the centimeter length scale are obtained. Angle-resolved photoemission spectroscopy measurements performed describe very well-resolved electronic band structure and spin orbit splitting of the bands at room temperature. Furthermore, the measurement reveals only two major domain orientations, indicating the successful growth of a highly crystalline and well-oriented MoS₂ monolayer.

Surface Science Division

Room 203C - Session SS+HC+MI-MoM

Dynamical Processes at Surfaces

Moderator: Gareth Parkinson, TU Wien

8:20am **SS+HC+MI-MoM-1 Light Induced Single-Molecule Dynamics at Surfaces, Wilson Ho**, University of California, Irvine **INVITED**

Inhomogeneity of different length scales is one of the fundamental characters of matter that has its origin in the spatial variations of the charge and mass distributions. While many changes in nature and in the laboratory can be observed with the naked eyes, ultimately the interactions that lead to these changes occur at the atomic scale. In addition, heterogeneity influences the time scale that transformations occur at different locations, and the average time may differ significantly from the local times. The desire to understand and control changes in the charge and mass distributions would require experimental tools that possess simultaneous spatial and temporal resolutions to reveal the heterogeneity. This joint Å-fs resolution can be achieved by the combination of a femtosecond laser with a low temperature scanning tunneling microscope (fs-STM) that probes chemical transformations of single molecules. These experiments demonstrate the fs-STM approach in probing the effects of heterogeneity in space and time on the chemical dynamics in single molecules.

9:00am **SS+HC+MI-MoM-3 Probing the Effects of Surface Structure on the Dissociative Chemisorption of Methane, Eric High¹**, *D Tinney*, *A Utz*, Tufts University

Vibrational state-resolved reactivity measurements reveal details of fundamental processes that impact reactivity in the field of heterogeneous catalysis. Insights into energy flow during reaction obtained from observations of non-statistical mode-specific and bond-selective enhancements observed for methane and its isotopologues on transition metal surfaces are one example. By providing reactive gas-molecules with precisely defined energy in well-defined energetic coordinates, state-selective experiments have also proven to be valuable probes of how surface atom motion affects overall reactivity. In this work, we will present vibrational state-resolved data collected via IR laser excitation of the antisymmetric stretch of supersonically expanded CH₄ gas molecules incident on a Ni(997) surface. We will focus on measurements investigating both the low and high incident energy regimes on this lightly stepped single crystal at a wide range of surface temperatures ($T_s = 120$ K to 1000 K). We will explore the possibility of benchmarking site-specific reaction barriers for dissociative chemisorption with molecules near the energy threshold for reaction. For higher energy molecular beams incident on higher surface temperatures, we will report on how the presence of steps on the Ni(997) surface modifies the kinetics of surface-bound C diffusion into the Ni subsurface and bulk and how this process impacts subsequent methane reactivity on this surface.

¹ Morton S. Traum Award Finalist

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9:20am **SS+HC+MI-MoM-4 Adsorption and Diffusion of NH₃ on Anatase-TiO₂ (101)**, *Kræn Christoffer Adamsen, S Koust, E Kolsbjerg, B Hammer, S Wendt, J Lauritsen*, Aarhus University, Denmark

Fundamental understanding of catalytic processes for NO_x removal (Selective Catalytic reaction, SCR) is vital for improving existing catalysts and developing new. In the SCR cycle, NO_x is known to react from gas-phase on adsorbed ammonia on VO_x/TiO₂ based catalysts, and adsorption of ammonia on such oxides is therefore of great importance for fundamental understanding of NO_x-removal and SCR catalysis. Here we present a fundamental study of the static and dynamic behaviour of ammonia on anatase-TiO₂ (101), the predominant facet on anatase-TiO₂ nanoparticles. High resolution Scanning Tunnelling Microscopy (STM) of static adsorbed ammonia molecules at room temperature, indicates a strong binding to the surface. Through synchrotron radiation XPS ammonia was found to adsorb molecularly. The strong binding of ammonia was further quantified by Temperature Programmed Desorption (TPD) which also shows a highly coverage dependent binding energy, indicating molecular repulsion. All experimental obtained results are in accordance with a proposed theoretically calculated DFT-model of ammonia absorption.

Next, single ammonia molecule diffusion measured utilizing the high-speed Aarhus STM, show diffusibility to all neighbouring sites. Molecular repulsion also show a clear effect on static structures, where nearest neighbouring site occupation is rarely observed. Statistical analysis of intermolecular coordination supplied repulsion energies, which agree with observed values in TPD spectra and theory. For diffusion, we conclude that molecular repulsion increases the diffusibility for higher coordinated ammonia molecules. However when two ammonia occupy two nearest neighbour sites, they have the possibility of diffusing through a rolling effect, where ammonia can move more easily in one direction, this phenomena has also been seen for water on other oxide surfaces. Our analysis thus shows a surprisingly complex diffusion behaviour of NH₃ on anatase TiO₂(101), which however resembles water dimer diffusion of water dimers on Rutile-TiO₂ (110).

9:40am **SS+HC+MI-MoM-5 Non-equilibrium Growth of Metastable Clusters as a Means of Controlling Supramolecular Structure.**, *Ryan Brown*, Clarkson University; *A Kandel*, University of Notre Dame

This poster will review the use of non-equilibrium growth conditions to produce supramolecular structures not easily accessible using traditional self-assembly approaches. Specifically, the formation of cyclic, hydrogen-bonded clusters at the vacuum-solid interface following the direct injection of a solution into a high vacuum chamber gives insight into the utility of employing non-equilibrium growth conditions for producing supramolecular structures with metastable configurations. When deposited in a rapidly evaporating droplet, hydrogen bonding small molecules can form clusters with 5-fold symmetry if the correct combination of hydrogen bonding groups are present. These features persist at room temperature, but evolve into more complex structures upon mild annealing. Initial studies of this phenomenon in ferrocenecarboxylic acid, 1,1'-ferrocenedicarboxylic acid, indole carboxylic acid, and isatin will be discussed. Finally, future systems and directions of study will be discussed.

10:00am **SS+HC+MI-MoM-6 Ultrafast Dynamics of Reaction Pathways on Metal Surfaces**, *Jerry LaRue*, Chapman University

Important chemical processes often occur on the femtosecond timescale, requiring the use of femtosecond excitation and probing techniques to study them. Optical femtosecond laser pulses are a convenient method of initiating catalytically important reactions on metal surfaces, such as CO hydrogenation and CO oxidation, on the femtosecond timescale. Using femtosecond x-ray pulses from free electron lasers (FEL), we have selectively probed the bond making and breaking processes of these reactions using O and C k-edge x-ray absorption and emission spectroscopies to obtain time-resolved electronic structure maps. These electronic structure maps reveal the time evolution of different surface species along the reaction pathway, providing new insights into the reaction dynamics on metal catalysis. This talk will highlight past and recent results in reaction dynamics on metal surfaces as investigated using femtosecond x-ray pulses and supported through density functional theory (DFT) calculations and *ab initio* molecular dynamics (AIMD) simulations. Specific systems include CO desorption CO oxidation, and CO hydrogenation on ruthenium.

10:40am **SS+HC+MI-MoM-8 Designer Solids via Multi-Heteroepitaxy: Layer-by-Layer Deposition of Molecular Frameworks on Solid Substrates**, *Christof Wöll*, Karlsruhe Institute of Technology, Germany **INVITED**

Realizing molecular "Designer Solids" by programmed assembly of building units taken from libraries is a very appealing objective. Recently metal-organic frameworks (MOFs) have attracted a huge interest in this context. Here, we will focus on MOF-based electrochemical [1,2], photoelectro-chemical [3] and photovoltaic devices [4,5]. Internal interfaces in MOF heterostructures are also of interest with regard to photon-upconversion [6] and can be used for the crosslinking of sandwiched, reactive monomers [7]. Since the fabrication of reliable and reproducible contacts to MOF-materials represent a major challenge, we have developed a layer-by-layer (lbl) deposition method to produce well-defined, highly oriented and monolithic MOF thin films on a number of different substrates. The resulting films are referred to as SURMOFs [8]. The fabrication of hetero-multilayers (see Fig. 1) is rather straightforward with this lbl method. In this talk, we will describe the principles of SURMOF fabrication as well as the results of systematic investigations of electrical [9] and photophysical properties exhibited by empty MOFs and after loading their pores with functional guests. Furthermore, we will discuss further applications realized by loading MOFs with nanoparticles or quantum dots.

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11:20am **SS+HC+MI-MoM-10 Isotope Enrichment via Non-Equilibrium Differential Condensation and Reflection using Supersonic Beam Gas-Surface Scattering**, *Jacob Graham, A McMillan, K Nihill, S Sibener*, University of Chicago

Isotopically enriched materials have a variety of uses including chemical labeling, energy, medicine, and quantum computing. To stimulate the further development of these applications, modern, efficient isotope enrichment methods are needed. Non-equilibrium supersonic beam gas-surface scattering and differential condensation is shown to be a new and broadly applicable route to isotope enrichment. This enrichment is demonstrated with ³⁶Ar and ⁴⁰Ar isotopes reflecting from low temperature condensates of argon, with differences arising in the condensation coefficient, which depend on the degree of collisional energy exchange for each isotope at the interface. The enrichment factors were found to be tunable as a function of incident beam kinetic energy. For example, ³⁶Ar was found to be *enriched* relative to ⁴⁰Ar in the scattered fraction by greater than a factor of two, for a seeded beam of argon in helium having incident velocity 1650 m/s. In a separate and complementary experiment under the same conditions, the amorphous argon condensate was found to be *depleted* in its ³⁶Ar content, confirming this effect. This observed isotope selectivity during deposition introduces a new method for isotopic enrichment and purification as well as *in-situ* isotopic materials engineering.

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11:40am **SS+HC+MI-MoM-11 Structural Reorganization of Sequentially Adsorbed Two-component Self-assembled Monolayers after Soft Ultraviolet Irradiation**, *C Gerber, Rebecca Quardokus*, University of Connecticut

Sequentially adsorbed anthracene dicarboxylic acid and octanethiol on Au(111) form ordered regions of octanethiol, gold vacancy islands, and areas of disorder near domain boundaries and vacancy islands. Vapor deposition of octanethiol after drop-cast deposition of anthracene dicarboxylic acid on Au(111) results in small $(\sqrt{3} \times \sqrt{3})R30^\circ$ and $c(4 \times 2)$ octanethiol domains. Initial exposure to soft ultraviolet irradiation increases disorder with only a few small close-packed octanethiol domains remaining. Repeated exposure to soft ultraviolet irradiation shows some removal of octanethiol molecules and sequential imaging by scanning tunneling microscopy gives snapshots of the stepwise reordering of the domains that ultimately leads to a structurally reordered monolayer consisting of larger domains of low-coverage octanethiol in a $p \times \sqrt{3}$ structure.

2D Materials Focus Topic

Room 201B - Session 2D+MI+NS-MoA

2D Materials Characterization including Microscopy and Spectroscopy

Moderators: Stephan Hofmann, University of Cambridge, UK, Richard Vanfleeter, Brigham Young University

1:20pm 2D+MI+NS-MoA-1 Observing the Mechanisms of Graphene Growth during Chemical Vapor Deposition: Routes to Controlling Layer Number and Domain Size, *Robert Weatherup*, University of Manchester, UK

INVITED

Chemical vapor deposition (CVD) on polycrystalline metal foils has emerged as the most economic and versatile means for producing 2D materials over large areas,¹ and directly integrating them with other device materials to achieve new functionality.² To tailor these materials to specific applications, a detailed understanding of the underlying growth mechanisms is required such that parameters such as domain size, defect density, and layer number can be precisely controlled. However, the elevated temperatures and reactive gas environments involved in growth make direct observation challenging, whilst ex situ measurements are often ambiguous.

Here we apply environmental scanning electron microscopy (ESEM) and ambient pressure X-ray photoelectron spectroscopy (APXPS) to directly observe graphene growth under realistic CVD conditions on polycrystalline Pt foils.³ This reveals a variety of processes involved in graphene formation including isothermal growth by direct hydrocarbon dissociation, isothermal dissolution into the catalyst bulk, and precipitation on cooling. The balance of these processes, and thus growth outcome, is shown to depend critically on the distribution of carbon close to the catalyst surface, which is in turn intimately linked to the processing profile. We thereby develop a growth model for graphene CVD that considers precursor dissociation, mass-transport, attachment to the edge of growing graphene domains.⁴ This is shown to be generally applicable to several transition metal catalysts,⁵ and serves as a general framework for understanding and optimizing the growth of 2D materials on polycrystalline catalysts.

We thus demonstrate that the CVD process can be rationally designed to yield different desired growth outcomes from the same polycrystalline starting catalyst, including uniform SLG with large domain sizes (>100 μm), large isolated BLG domains (>50 μm), and uniform BLG. Our results show that through targeted operando experiments the influence of key process parameters can be established, enabling precise control over 2D material growth including domain sizes and layer number.

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2:00pm 2D+MI+NS-MoA-3 Band Alignment of 2-D Materials by Internal Photoemission, *Q Zhang, S Zhang*, Theiss Research & National Institute of Standards and Technology; *B Sperling, Nhan Nguyen*, National Institute of Standards and Technology

Two-dimensional (2-D) materials have brought new possibilities for the future electronic and optoelectronic applications [1], [2]. Electronic band alignment at the interface is one of the important parameters in many device designs. For instance, staggered band alignment is preferred to separate photon generated electron-hole pairs in optoelectronic and photovoltaic devices [3]. For the 2-D materials in the monolayer (ML) limit, it has been a challenge to accurately measure the electron affinity which determines how the bands align at the interface. In fact, most 2-D heterojunctions are designed using calculated or theoretically predicted band alignments [4]. In this work, we present an experimental measurement using internal photoemission spectroscopy (IPE) to determine the band offset of MX₂ semiconductors (M = Mo, W; X = S, Se) in relative to an oxide barrier and suggest possible combination of the MX₂ materials to be used for optoelectronic and photovoltaic applications. This IPE approach is seen as a unique method that can be applied to characterize other 2-D materials.

The IPE test structure is fabricated by exfoliating MX₂ flakes on to the Al₂O₃/p⁺Si substrate and depositing Ti/Pt contacts on the flakes with large open areas for light absorption. By using gold film mediated exfoliation method [5], large area (> 75 x 75 μm^2) ML MX₂ flakes are obtained, confirmed by Raman spectrum and photoluminescence mapping.

Photocurrents of the MX₂-Al₂O₃-p⁺Si structure are measured with the incident photon energy swept from 2.0 eV to 5.5 eV and gate voltage V_{GS} (applied to the Si back gate) stepped from -1.0 V to 1.6 V. The oxide flat band voltage (V_{FB}) is extracted by the voltage where the photocurrent switches sign near and above photoemission thresholds. The band offsets at the MX₂/Al₂O₃ and Al₂O₃/Si interfaces are extracted as the thresholds of the cube root of photoemission quantum yield (Y) being the ratio of the photocurrent over the incident light flux [6]. At gate bias below V_{FB} , the band offset between Al₂O₃ and Si is measured and found to be 3.4 eV for all the 4 devices, which is also a well-established value. More importantly, the band offset at the MX₂/Al₂O₃ interfaces combined with the known optical band gaps of ML MX₂ suggest that MoS₂/WS₂ and MoSe₂/WSe₂ can possibly form the staggered heterojunction.

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2:20pm 2D+MI+NS-MoA-4 Visible to mid-IR Nanoscale Characterization of 2D Materials via Photo-induced Force Microscopy, *Pdraic O'Reilly, D Nowak, S Park*, Molecular Vista

While several 2D materials have been studied with scattering scanning near-field optical microscopes (s-SNOM) with nanoscale spatial resolution, most have focused on the study of surface phonon polariton (SPP) [1]. In this paper, we introduce a relatively new technique called photo-induced force microscopy (PiFM), which combines atomic force microscope (AFM) and broadband optical spectroscopy to analyze both topography and polarizability of samples with sub-10 nm spatial resolution [2]. With PiFM, the near-field optical information is acquired by measuring the photo-induced force between the AFM tip and the sample rather than by collecting photons with a far-field photo-detector; this near-field excitation and near-field detection configuration provides excellent signal-to-noise without the far-field background signal from the much larger focal spot, making the technique robust and easy-to-use. With mid-IR sources, PiFM can image nanoscale SPP as with s-SNOM. With supercontinuum visible-infrared light source, it can directly probe the exciton resonances with equally impressive spatial resolution. With its capability to image number of layers, quality of samples, and plasmonic fields, PiFM is an ideal nanoscale characterization tool for wide range of 2D materials. Results from graphene, MoS₂, WS₂, and hBN will be presented.

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2:40pm 2D+MI+NS-MoA-5 Polymorphic Structures and Diversified Properties of Low-dimensional Materials Investigated by In situ Electron Microscopy, *Kazu Suenaga*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

INVITED

Two-dimensional transition metal dichalcogenides (TMDs), consisting of an atomic plane of a transition metal (M: Ti, Nb, Mo, Re, etc.) sandwiched between two chalcogen atomic planes (X: S, Se, Te). This crystalline structure combined with a wide variety of constituent elements give rise to diverse electronic properties, strongly governed by the number of its *d*-orbital electrons. MoS₂ and WS₂ are the most representative “group 6” TMDs featuring trigonal prismatic (H) phase semiconductor with a direct band gap. The TMDs can exhibit various polymorphs and present different electronic properties as the atomic arrangement changes originating from charge transfer. A metallic octahedral (T) phase has been reportedly stabilized by alkali metal intercalation [1], and another distorted octahedral phase zigzag-shape phase (Z) with clusterization of metal atoms into zigzag chains by using solvent-based exfoliation. Some simulations indicate that the Z phase may undergo the Peierls distortion and be transformed into a diamond-shape (DS) phase where atoms reconstruct in a way that four metal atoms appear as a diamond (rhombus) in the plane [2]. We show in this talk the experimental evidences for these polymorphic structures and diversified properties found in a family of 2D TMDs.

These monolayer forms in TMDs are typically the same as a single layer of the bulk material. However, PdSe₂ presents a puzzle. Its monolayer form has been theoretically shown to be stable, but there have been no reports that monolayer PdSe₂ was fabricated. Here, we demonstrate that the preferred monolayer form of this material amounts to a melding of two

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bulk monolayers accompanied by the emission of Se atoms so that the resulting stoichiometry is Pd₂Se₃[3].

[1] Y.-C. Lin, D. O. Dumcenco, Y.-S. Huang and K. Suenaga, *Nature Nanotechnology*, 9 (2014) pp.391-396

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[3] J. Lin, S. Zuluaga, P. Yu, Z. Liu, S. T. Pantelides, and K. Suenaga *Phys. Rev. Lett.*, 119 (2017) 016101

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3:40pm **2D+MI+NS-MoA-8 Probing Interlayer Interaction in van der Waals Materials by Low-energy Electron Microscopy (LEEM)**, *Johannes Jobst*, D Geelen, Leiden University, Netherlands; *R Tromp*, IBM, T.J. Watson Research Center; *S van der Molen*, Huygens-Kamerlingh Onnes Laboratory, Netherlands

INVITED

Knowledge on the interaction between layers is crucial to tailor the properties of van der Waals (vdW) materials. We investigate these using newly developed techniques based on low-energy electron microscopy (LEEM). With LEEM, we probe the reflection of electrons as a function of incoming energy (0-100 eV). We have recently extended our UHV instrument to also measure low-energy electron transmission (eV-TEM).

We apply LEEM and eV-TEM to few-layer graphene. With each layer, an unoccupied interlayer state is added, which hybridizes with the other states. In LEEM, the resulting eigenstates appear as minima in the reflection spectrum. In transmission, they show up as maxima. From both functions, we determine the hybridization energies of the interlayer states, which extend in 2D.

Next, we study the 2D-dispersion relations of these states. For that, we have developed *angle-resolved reflected-electron spectroscopy* (ARRES) [1]. With ARRES, we investigate few-layer graphene, hBN, as well as their combination. For the latter case we find negligible interaction. [2]

[1] Jobst *et al.*, *Nat. Comm.* **6**, 8926 (2015)

[2] Jobst *et al.*, *Nat. Comm.* **7**, 13621 (2016)

4:20pm **2D+MI+NS-MoA-10 Fast Full Wafer Analysis for Graphene and 2D-materials by Imaging Ellipsometry**, *Sebastian Funke*, Accurion GmbH, Germany; *P Braueniger-Weimer*, *S Hofmann*, University of Cambridge, UK; *P Thiesen*, Accurion GmbH, Germany

By combining the resolution of optical microscopy and the sensitivity of thin films, imaging ellipsometry (IE) is a powerful tool to characterize thin materials. It allows to measure monolayers of 2D-materials but also to visualize these monolayers on arbitrary substrates. It overcomes the need of specially tuned SiO₂ thicknesses to visualize e.g. Graphene in an optical microscope.

In the talk we present [1], the characterization of Graphene throughout all stages of the manufacturing process from the growth on Cu-foil up to the transferred sample on Si wafers. Unlike other methods IE directly visualizes graphene on the rough Cu. We apply IE to resolve a large area map of Graphene on Cu. The Graphene is directly characterized on the Cu-foil, no oxidation of the Cu is needed. To overcome the waviness of the foil, an autofocus algorithm is developed and applied.

IE is also able to distinguish a Graphene monolayer and hBN monolayer after the transfer process to a Si/SiO₂ substrate. We show large area map of the transferred sample. The contrast mode of IE is able to distinguish the different regions: (a) substrate only, (b) hBN only, (c) Graphene only and (d) an overlapping region of hBN and Graphene. The complete sample approx. 1cm x 0.8 cm is recorded in less than 6 minutes and shows defects and wrapping of hBN of a size as small as 4 μm.

Lastly, we apply IE to characterise full 4" wafers of graphene on Si.

[1] Braueniger, Funke *et al.* submitted

Magnetic Interfaces and Nanostructures Division

Room 201A - Session MI+2D+EM+NS-MoA

IoT Session: Symposium on new Magnetic Materials, Devices and Concepts for the Information Society

Moderator: Hendrik Ohldag, SLAC National Accelerator Laboratory

1:20pm **MI+2D+EM+NS-MoA-1 "ZOOMING in on Data Storage and the Superb HDD"**, *Roger Wood*, Western Digital

INVITED

Get ready for a wild ride starting with the vast distances of outer space and ending with the tiny

distances that separate atoms. For a very different perspective on data storage, each slide in the

presentation looks at things on a scale that is a factor of ten smaller than the previous slide. The

common thread is the technology of information storage. Information storage is what defines human

history and it is the machine-readable data storage developed in the last half-century that provides the

foundation of the modern information age. More than anything, data storage implies magnetic

recording and the hard disk drive. The humble Hard Disk Drive contains such exquisite technologies

and operates at such astounding precision that it almost defies belief. Yet, our industry churns out

these devices by the hundreds of millions and sells them for a few tens of dollars each. Please enjoy

this light-hearted logarithmic romp through storage technology from interstellar space to interatomic

spacings.

(The presentation is based on a talk given at the annual ASME ISPS banquet in Santa Clara, California, in June 2016, while the author was with Western Digital Corporation.)

2:00pm **MI+2D+EM+NS-MoA-3 Physics and Applications of Spin-transfer Torques**, *Andrew Kent*, New York University

INVITED

The magnetization of a magnetic material can be reversed by using electric currents that transport spin angular momentum [1]. This was predicted in magnetic tunnel junctions—two metallic ferromagnetic layers separated by a thin insulating barrier—by John Slonczewski in 1989 and demonstrated experimentally about a decade later. This discovery has had an enormous impact on magnetism research and technology [2], as prior to this the primary means to reorient the magnetization of a magnet was by applying magnetic fields (dating to 1819 and Oersted!). In this talk I will highlight some of the physics and applications enabled by the discovery of spin-transfer torques. This includes recent experiments that create localized spin-wave excitations (magnons droplets) in thin films with uniaxial magnetic anisotropy [3]. Spin-transfer torques also permit study of magnetic analogues of superconductivity, superfluidity and the Josephson effect that promise to increase our understanding of collective quantum effects. They may even enable braiding Majorana fermions [4]. Finally, I will discuss spin-torque switching of perpendicularly magnetized magnetic tunnel junctions [5], the basic device used in spin-transfer torque magnetic random access memories.

[1] A. Brataas, A. D. Kent and H. Ohno, "Current-Induced Torques in Magnetic Materials," *Nature Materials* **11**, 372 (2012)

[2] A. D. Kent and D. C. Worledge, "A new spin on magnetic memories," *Nature Nanotechnology* **10**, 187 (2015)

[3] D. Backes, F. Macia, S. Bonetti, R. Kukreja, H. Ohldag and A. D. Kent, "Direct Observation of a Localized Magnetic Soliton in a Spin-Transfer Nanocontact," *PRL* **115**, 127205 (2015)

[4] Alex Matos-Abiaguea, Javad Shabani, Andrew D. Kent, Geoffrey L. Fatina, Benedikt Scharfa, Igor Žutić, "Tunable magnetic textures: From Majorana bound states to braiding," *Solid State Communications* **262**, 1 (2017)

[5] C. Hahn, G. Wolf, B. Kardasz, S. Watts, M. Pinarbasi, A. D. Kent, "Time-resolved studies of the spin-transfer reversal mechanism in perpendicularly magnetized magnetic tunnel junctions," *Physical Review B* **94**, 214432 (2016)

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*Work done in collaboration with Dirk Backes, Gabriel Chaves, Daniel Gopman, Christian Hahn, Jinting Hang, Yuming Hung, Ferran Macia, Daniele Pinna, Laura Rehm, Debangsu Roy, Javad Shabani and Volker Sluka at NYU; Georg Wolf, Bartek Kardasz, Steve Watts and Mustafa Pinarbasi at Spin Transfer Technologies Inc.; and Hendrik Ohldag at SSRL

2:40pm **MI+2D+EM+NS-MoA-5 Hybrid Magnetic Heterostructures**, *Ivan K. Schuller*, *A Basaran*, University of California, San Diego; *J de la Venta*, Colorado State University; *J Ramirez*, Universidad de los Andes, Colombia; *T Saerbeck*, Institute Laue-Langevin, France; *I Valmianski*, University of California, San Diego; *X Batlle*, University of Barcelona, Spain **INVITED**

Hybrid materials allow the engineering of new material properties by creative uses of proximity effects. When two dissimilar materials are in close physical proximity the properties of each one may be radically modified or occasionally a completely new material emerges. In the area of magnetism, controlling the magnetic properties of ferromagnetic thin films without magnetic fields is an on-going challenge with multiple technological implications for low-energy consumption memory and logic devices. Interesting possibilities include ferromagnets in proximity to dissimilar materials such as antiferromagnets or oxides that undergo metal-insulator transitions. The proximity of ferromagnets to antiferromagnets has given rise to the extensively studied Exchange Bias[1].

In a series of recent studies, we have investigated the magnetic properties of different hybrids of ferromagnets (Ni, Co and Fe) and oxides, which undergo metal-insulator and structural phase transitions. Both the static as well as dynamical properties of the ferromagnets are drastically affected. Static properties such as the coercivity, anisotropy and magnetization [2-3] and dynamical properties such as the microwave response are clearly modified by the proximity effect and give rise to interesting perhaps useful properties.

Work supported by US-AFOSR and US-DOE

Selected References:

[1] *Exchange Bias*, Josep Nogues and Ivan K. Schuller, *J. Magn. Mater.* **192**, 203 (1999).

[2] *Control of Magnetism Across Metal to Insulator Transitions*, J. de la Venta, Siming Wang, J. G. Ramirez, and Ivan K. Schuller, *App. Phys. Lett.* **102**, 122404 (2013).

[3] *Coercivity Enhancement in V_2O_3 /Ni Bilayers Driven by Nanoscale Phase Coexistence*, J. de la Venta, Siming Wang, T. Saerbeck, J. G. Ramirez, I. Valmianski, and Ivan K. Schuller, *Appl. Phys. Lett.* **104**, 062410 (2014).

[4] *Collective Mode Splitting in Hybrid Heterostructures*, Juan Gabriel Ramirez, J. de la Venta, Siming Wang, Thomas Saerbeck, Ali C. Basaran, X. Batlle, and Ivan K. Schuller, *Phys. Rev. B*, **93**, 214113 (2016).

3:40pm **MI+2D+EM+NS-MoA-8 Organismic Materials and Intelligence**, *Shriram Ramanathan*, Purdue University **INVITED**

Intelligence in the natural world is panspermic to life, ranging from basic survival skills in non-neural organisms to co-operative foraging and complex mating strategies in higher level animals. We ask the question whether such remarkable features can be implemented in the physical world utilizing adaptive matter. We have identified strongly correlated semiconductors, one class of quantum materials as particularly suited for this effort, owing to their remarkable electronic plasticity. One may refer to these systems as organismic materials that display certain well-defined characteristics of living beings. In this presentation, we will present examples from the animal kingdom focusing on intelligence and episodic memory. Then we will discuss recent collaborative studies on correlated oxides demonstrating ancestral intelligence. We will conclude with examples of neural networks that can be designed with quantum materials that can replicate fundamental animal learning traits. The role of defects, strain and orbital occupancy control in design of electronic plasticity will be highlighted.

Thin Films Division

Room 102A - Session TF+EM+MI+PS-MoA

Thin Films for Advanced Memory Applications and Magnetics

Moderator: Robert Grubbs, Sandia National Laboratories

1:40pm **TF+EM+MI+PS-MoA-2 ---Multiferroic Integration of Undoped Ferroelectric HfO_2 and Ferrimagnetic $CoFe_2O_4$ Thin films by Radical-Enhanced Atomic Layer Deposition**, *J Chang*, *Adrian Acosta*, *J Chang*, University of California at Los Angeles

Multiferroic materials that exhibit the coexistence and coupling between ferroelectricity and magnetism are of great interest due to their potential for enabling next-generation memories. To overcome the scarcity and weak response of intrinsic multiferroics, composite strategies were proposed to realize robust multiferroic behavior by coupling the properties from constituent ferroelectric and magnetic phases. However, additional challenges for an applicable multiferroic composite are present in the ferroelectric phase since conventional perovskite-based ferroelectrics lack the necessary electrical stability and silicon-compatibility for device integration.

Orthorhombic ferroelectric HfO_2 (FE- HfO_2) based thin films have emerged in the field of microelectronics research owing to its superior compatibility with CMOS technology as well as desirable electrical properties. In this work, multiferroic integration of undoped FE- HfO_2 thin films and ferrimagnetic $CoFe_2O_4$ (CFO) on Si substrates via radical-enhanced atomic layer deposition (RE-ALD) are first demonstrated. For the RE-ALD process, atomic oxygen was utilized in conjunction with TDMAHf and TMHD-based metalorganic precursors for the growth of HfO_2 and CFO respectively. In the composite design, CFO acts as a mechanical constraint to stabilize FE- HfO_2 as well as an active magnetic layer.

Composite ferroelectricity was studied as a function of FE- HfO_2 film thickness as well as post-deposition annealing temperatures. Film crystallinity was investigated through the use of a synchrotron beam source to understand the structural evolution. The induced ferroelectricity was observed to correlate with HfO_2 orthorhombic phase and was maximized when HfO_2 is ~ 6 nm and after annealing at ~ 700 - 800 °C. CFO/FE- HfO_2 composites showed ferroelectric behavior with remnant polarization ~ 5.5 $\mu C/cm^2$ and electrical coercivity ~ 340 - 2000 kV/cm, with the potential to be further enhanced via the inclusion of dopants. Comparable magnetism was observed with out-of-plane anisotropy, a saturation magnetization of ~ 155 emu/cm³, and a magnetic coercivity ranging from ~ 1000 - 3400 Oe. Piezoresponse force microscopy (PFM) verified the strain interaction in the CFO/FE- HfO_2 design. Lastly, a magnetoelectric coupling coefficient of $\sim 5.5 \times 10^{-8}$ s/m (~ 55 Oe cm/kV) was obtained from the multiferroic structure with 6-nm thick HfO_2 layer via an *ex situ* poling SQUID magnetometer setup. This work not only highlights the potential of FE- HfO_2 based multiferroic composites in realizing magnetoelectric spintronic devices but also unveils the possibility of utilizing alternative capping layers for achieving multifunctional composite heterostructures.

2:00pm **TF+EM+MI+PS-MoA-3 Growth and Characterization of BeO Thin Films Grown by Atomic Layer Deposition using H_2O and O_3 as Oxygen Sources**, *Lee Woo Chul*, *C Cheol Jin*, Center for Electronic Materials, Korea Institute of Science and Technology, Korea; *K Sangtae*, Center for Electronic Materials, Korea Institute of Science and Technology, Korea; *L Eric S.*, *Y Jung Hwan*, Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), South Korea; *H Cheol Seong*, Department of Materials Science and Engineering, and Inter-University Semiconductor Research Center, College of Engineering, Seoul National University, South Korea; *B Christopher W.*, Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), South Korea; *K Seong Keun*, Center for Electronic Materials, Korea Institute of Science and Technology, Korea

BeO has a very large band gap (10.6 eV), which is even larger than that of representative large band gap materials; SiO_2 (~ 9 eV) and Al_2O_3 (~ 8 eV). BeO thin films reveal high quality of the interface with Si and semiconductors, showing a possibility as a gate dielectric. Furthermore, rocksalt BeO was recently predicted to have a very high dielectric constant (~ 275) and a very large band gap (10.6 eV). However, the fascinating dielectric properties have not been experimentally realized yet because of the instability of the rocksalt BeO. Nowadays, atomic layer deposition (ALD) is a common technique for film growth in a semiconductor industry. The ALD process of the BeO thin films is necessary to be developed to

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implement BeO in the semiconductor industry. Herein, the growth characteristics and properties of BeO thin films grown by ALD are investigated. We demonstrated that ALD chemistries between dimethylberyllium (DMB) and two different oxygen sources, H₂O and O₃, are governed by different reaction mechanisms, resulting in different film properties.

BeO thin films were grown in a traveling-wave type reactor by ALD with DMB and different oxygen sources, such as H₂O and O₃, in the temperature range of 150 to 300 °C. Although H₂O-ALD and O₃-ALD of BeO all showed self-saturation behavior, the growth behavior and film properties are strongly dependant on the oxygen sources. With increasing growth temperatures, the growth per cycle (GPC) of H₂O-ALD of BeO decreases, while that of O₃-ALD of BeO is almost constant. The properties of the BeO films grown in H₂O-ALD are nearly temperature-independent, whereas the BeO films grown in O₃-ALD at low temperatures (< 200 °C) reveal high impurity concentrations and a low film density. These cause lowering of the band gap and dielectric constant of the BeO films grown by O₃-ALD at low temperatures. These findings demonstrate that the O₃-ALD process requires relatively more thermal energy than H₂O-ALD does, to produce high-quality BeO thin films.

2:20pm TF+EM+MI+PS-MoA-4 Atomic Layer Deposition of Magnetic Films and Patterned Features with Tunable Magnetic Properties, Z Zhang, John Ekerdt, University of Texas at Austin

We report a process to generate carbon-free Co metal films and patterns by first growing films of CoO via atomic layer deposition on various hydroxylated surfaces and then reducing the CoO at low temperatures to Co metal. The CoO ALD process employs (bis(N-tert butyl), N'ethylpropionamidnato) cobalt (II) and water at 180 °C. Similar processes work for Fe and Ni growth. The metal oxides have a lower density than the metal and will spread uniformly over oxide substrates whereas ultra-thin metal films tend to dewet from the oxide and generate discontinuous films. This dewetting is a strong function of temperature and can be mitigated by lowering the temperature of the reduction process or by lowering the energy of the free surface. Temperatures in excess of 420 °C are required to achieve full reduction of 4.5-nm CoO in H₂ (or D₂); films reduced at this temperature are discontinuous. We report the use of atomic deuterium that is generated over a heated tungsten filament and show that we can fully reduce 4.5-nm CoO to Co at 220 °C without the metal film dewetting oxides such as SiO₂, MgO, ZrO₂, and Al₂O₃. Thermal history of the film is critical to tuning the magnetic properties. As ultra-thin films roughen by extended annealing at 200 °C the film coercivity can be manipulated from 90 to 500 Oe. Since the CoO ALD process is initiated on hydroxylated surfaces and can be blocked by organic films, we pattern polystyrene using UV crosslinking through a shadow mask or a diblock co-polymer to generate features ranging from microns to tens of nanometers and deposit CoO on the hydroxylated surfaces that are opened in the polystyrene. This presentation will address the interface issues in achieving selective growth and in manipulating the magnetic properties of continuous Co films and shaped features.

2:40pm TF+EM+MI+PS-MoA-5 Tuning of the Magnetic and Electronic Properties of Epitaxial Heusler Compound Heterostructures, Christopher Palmström, University of California, Santa Barbara

Heusler compounds have received a lot of attention because of their large range of properties. Their properties depend on the number of valence electrons per formula unit and have been predicted to be semiconductors, metals, ferromagnets, antiferromagnets, half metals, superconductors and topological insulators. Similar to compound semiconductors, the band structure and lattice parameters of Heusler alloys can also be tuned through alloying but over a much larger range of properties. Magnetic tunnel junctions using Heusler alloys that are predicted to be half metals have shown record tunneling magnetoresistance. Heusler half metals have been predicted to have very low Gilbert damping coefficients. They can also be lattice matched to most compound semiconductors and have been used for spin injecting contacts. Recent theoretical predictions suggest that atomic level Heusler superlattices can result in half metallicity and perpendicular magnetization. This presentation will emphasize the molecular beam epitaxial growth combined with in-situ and ex-situ structural, electronic and magnetic characterization of Heusler heterostructures on III-V semiconductors and MgO single crystal substrates. Tuning of their magnetic and electronic properties through elemental substitution to change the number of valence electrons per formula unit and atomic level superlattice growth will be discussed. Examples of Heusler heterostructures and controlling of their magnetic and

electronic properties include tuning of the spin polarization in Co₂Mn_{1-x}Fe_xSi, Heusler contacts for spin injection into GaAs, spin polarization and magnetic anisotropy of Co₂MnAl/Fe₂MnAl atomic scale superlattices, substitution with Fe in CoTiSb with the aim to convert a semiconductor to half metal and interfacial reactions at Co₂MnSi/MgO interfaces. By careful tuning of the half metallic Heusler film composition, Gilbert damping coefficients <0.001 have been observed.

3:40pm TF+EM+MI+PS-MoA-8 Stabilization of Ferroelectric Phase of Hf_{0.5}Zr_{0.5}O₂ on NbN at 4 K, Michael David Henry, S Smith, R Lewis, Sandia National Laboratories; J Ihlefeld, University of Virginia

This work demonstrates cryogenic ferroelectric behavior of atomic layer deposited (ALD) hafnium zirconium oxide (HZO) using reactively sputtered niobium nitride electrodes. With the discovery of ferroelectricity in doped HfO₂, perturbations of the dopants expanded from silicon into mixtures utilizing yttrium and zirconium and with electrodes ranging from platinum to nitrides such as titanium nitride and tantalum nitride. This set of materials have demonstrated stabilizing a crystalline phase permitting both ferroelectric and anti-ferroelectric behaviors to have been observed. With the atomic similarities between Ta and Nb, a natural extension the electrode materials' set to include NbN was explored in this work.

Devices tested at both room temperature (RT) and under cryogenic conditions demonstrated ferroelectric behavior as determined by polarization vs. electric field (P-E) loops. The polarization results show comparable ferroelectric behavior at room temperature and 4 K, however the effect of the dielectric polarization is combined with the remnant polarization (P_r) in this measurement. To separate the two effects, remnant polarization sweeps were performed and plotted only displaying the P_r. A typical measurement on a 170 mm diameter device, was performed starting at 4 K and ending at 150 K. By adding the positive and negative P_r with the electric field at 0 MV/cm (2P_r), polarization was observed to decrease as the stage was warmed up. A second known behavior of ferroelectrics is the so-called wake-up effect where the ferroelectric phase is understood to be stabilized by oxygen movement as a positive and negative voltage is applied. Here, a 3 V square wave at 1Hz was utilized in 60 second intervals with P_r loops performed before and after each wake-up cycling at room temperature. The 2P_r was seen to come to steady state after approximately 100 seconds. Remnant polarization at the conclusion of 360 seconds is seen to have polarization approximately 10 mC/cm², a value comparable to other findings. Polarization values of approximately 10 mC/cm² suggest that these ferroelectric films could be utilized with superconductors at liquid He temperatures for a new class of superconductor-ferroelectric based devices.

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. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

4:00pm TF+EM+MI+PS-MoA-9 Atomic Layer Deposition of Co/Pt Multilayer films for Perpendicular Magnetic Anisotropy, Devika Choudhury, A Mane, C Phatak, A Petford Long, J Elam, Argonne National Laboratory

"Smaller, Faster and Efficient" are the key words describing the ever increasing need of data-storage industry.^[1] This demand has brought about a shift from longitudinal recording in magnetic media to perpendicular recording, where magnetic bits are perpendicular to the plane of the recording media instead of being in the same plane. Significantly higher storage density is obtained as a result of using the perpendicular magnetic recordings utilizing materials demonstrating perpendicular magnetic anisotropy (PMA). Strong PMA is usually observed in ultrathin films of ferromagnetic metals like Co and Fe forming alloys with heavy metals like Pt, Pd, Au and Ta.^[2] Of them Co/Pt alloys and multilayer structures are probably the most widely investigated system for understanding the PMA origin and behavior.

The effective anisotropy energy of the multilayer films in the PMA regime depends on various factors like thickness of the individual Co/Pt layers, quality of interfaces and crystallinity of the films.^[3] Till date, the commonly used techniques for growth of Co/Pt multilayers have been electron beam evaporation and sputtering. However, for development of higher areal density using three-dimensional media, conformal, uniform and controlled deposition of the thin films is certainly required.

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In this work, we utilize atomic layer deposition (ALD) of Co/Pt multilayers to overcome limitations of the other growth processes. ALD provides precise control over the film thickness along with uniform and conformal films thus resulting in distinct sharp interfaces between the individual metal films. Bis(N-t-butyl-N'-ethylpropanimidamido)cobalt(II) and hydrogen precursors are used for Co ALD while Trimethyl(methylcyclopentadienyl)platinum(IV) and water are used as precursors for Pt deposition. QCM studies confirm self-limiting ALD growth nature of the individual metal films at 300°C. Pt(10nm)/[(Co/Pt)x8](16nm)/Pt(2nm) stacks are grown using alternate cycles of Co and Pt. QCM measurements reveal a short nucleation regime of Pt over Co films. HRTEM imaging and XPS analysis of the multilayer stacks are utilized to study the interfaces of the multilayer films closely. Preliminary SQUID measurements show a change in anisotropy between pure Co and Co/Pt multilayer films. Effects of variation in individual layer thicknesses, deposition temperature, post-deposition annealing temperature etc. remains to be seen.

References:

- [1] B. Tudu and A. Tiwari, *Vacuum*, 146, 329 (2017).
- [2] V. M. Parakkat, K. R. Ganesh, and P. S. A. Kumara, *AIP Advances*, 6, 056118 (2016).
- [3] B. F. Vermeulen, J. Wu, J. Swerts, and S. Couet et al. *Journal of Applied Physics*, 120, 1639031 (2016).

2D Materials Focus Topic

Room 201B - Session 2D+EM+MI+NS-TuM

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

Moderator: Johannes Jobst, Leiden University

8:00am **2D+EM+MI+NS-TuM-1 Effect of Lattice Stacking Orientation and Local Thickness Variation on the Mechanical Behavior of Few Layer Graphene Oxide**, *Teng Cui, S Mukherjee, C Cao, P Sudeep, J Tam*, University of Toronto, Canada; *P Ajayan*, Rice University; *C Singh, Y Sun, T Filleter*, University of Toronto, Canada

Investigation of few layer 2D materials is fundamentally important to bridge the gap between monolayer and bulk properties, and practically meaningful for applications as reinforcement nanofillers and layered electronic devices. Few layer introduces differences from intrinsic properties of monolayers due to the complexity of structural heterogeneities, such as lattice stacking orientation and local thickness variation. In this work [1], few layer graphene oxide (GO) with different structural heterogeneities were studied using atomic force microscopy-based deflection measurements and transmission electron microscopy (TEM). Direct TEM evidence of fracture surfaces and molecular dynamics (MD) simulations revealed decoupled and dissimilar layer crack patterns (i.e., different cracking pathway of top and bottom layers) for misaligned bilayer GO. In contrast, aligned GO bilayers generally fractured with a larger portion of common cracks shared by both layers, indicating stronger interlayer interaction than its misaligned counterpart. MD results also revealed insignificant effect of lattice alignment on the strength and toughness of GO bilayers, which is ~ 23.5 GPa and $\sim 1.71 \times 10^{-18}$ J/nm³, respectively, for both aligned and misaligned cases. Scaling up to ~ 5 layers and above revealed more significant local thickness heterogeneity and consequently a $\sim 60\%$ reduction of the normalized fracture force and toughness with respect to the average number of layers. MD simulations on partially intercalated few layer GO revealed anisotropic and heterogeneous stress distributions, as well as stress concentration near the inner edges, which may account for the significant reduction of strength and toughness.

[1] T. Cui, S. Mukherjee, C. Cao, P. M. Sudeep, J. Tam, P. M. Ajayan, C. V. Singh, Y. Sun, and T. Filleter, "Effect of Lattice Stacking Orientation and Local Thickness Variation on the Mechanical Behavior of Few Layer Graphene Oxide", *Carbon*, accepted.

8:20am **2D+EM+MI+NS-TuM-2 Out-of-Plane Mechanical Properties of 2D Hybrid Organic-Inorganic Perovskites by Nanoindentation**, *Qing Tu, I Spanopoulos, S Hao, C Wolvertson, M Kanatzidis, G Shekhawat, V Dravid*, Northwestern University

2D layered hybrid organic-inorganic perovskites (HOIPs) have demonstrated improved stability and promising photovoltaic performance. The mechanical properties of such functional materials are both fundamentally and practically important to achieve both high performance and mechanically stable (flexible) devices. Here we report the static, out-of-plane mechanical properties of a series of 2D layered lead iodide HOIPs with a general formula of $(R-NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$, and investigate the role of structural sub-units (e.g., the length of the organic spacer molecules -R and the number of inorganic layer -n) on the mechanical properties by nanoindentation. We find that the 2D HOIPs are softer than their 3D counterparts due to the replacement of the strong inorganic layer and ionic bonds by the soft organic layers and the weak Van der Waals interactions. As n increases from 1 to 5, the relative amount of these weak factors in the crystals are decreasing and both the out-of-plane Young's modulus E and hardness H increase, approaching to the reported values of corresponding 3D crystals. DFT simulations showed a similar trend to the experimental results. Furthermore, we show that increasing the alkyl chain spacer molecule -R from -C₄H₉ to -C₁₂H₂₅, E first decreases and eventually plateaus while no clear trend in H is observed. Our results reveal that the competition between the stiff inorganic layers, the soft organic layer and the weak Van der Waals interfaces determines the mechanical properties of 2D HOIPs. Finally, we compare these findings with those in other 2D layered materials such as h-BN, MoS₂ and MXene, and shed light on routes to further tune the out-of-plane mechanical properties of 2D layered HOIPs.

8:40am **2D+EM+MI+NS-TuM-3 Mechanical Properties of Many-layer CVD Graphene**, *Kyle Larsen, S Lehnardt, J Rowley, B Anderson, R Vanfleet, R Davis*, Brigham Young University

Graphene, a monoatomic layer of carbon atoms, has a reported Young's modulus of 1 TPa and a tensile strength of 130 GPa. These values make it both the strongest and one of the stiffest materials ever reported. The mechanical properties of multilayer graphene grown by chemical vapor deposition have been reported for films of up to 10 layers (3.35 nm). Films thicker than about 10 layers (sometimes considered graphite rather than multilayer graphene) are of interest as membranes and in MEMS applications. We have characterized CVD grown many-layer graphene films with thicknesses of about 50 nm by Raman spectroscopy, burst testing, and atomic force microscopy. The atomic force microscope was used to map the local compliance over suspended regions containing cantilevers cut out of the many-layer graphene with a focused ion beam. Analytical and finite element modeling were used in the analysis of the deflection of the many-layer graphene cantilevers to extract Young's modulus. The many-layer graphene is high quality (little or no D peak in the Raman spectrum) and has a Young's modulus in the range reported for graphene (0.5 TPa to 1 TPa).

9:00am **2D+EM+MI+NS-TuM-4 Electronic Structure and Magneto-transport Properties of Nanostructured Graphene on SiC(001)**, *Victor Aristov*, DESY Hamburg, Germany; *H Wu*, BIT, Beijing, China; *O Molodtsova*, DESY Hamburg, Germany; *A Chaika*, ISSP RAS, Russia

Graphene shows unbelievable properties that are of worth both for basic investigations and technology. The aptitude to open gap and to get graphene magnetic are principal challenges in the fields of up-to-date applications. Nanostructured graphene with an enormous amount of nanodomain boundaries and ripples becomes to be the most promising material for graphene-based electronic and spintronic applications, since nanodomain edges can completely reflect electrons over a great range of energies [1] and hold spin-polarized electronic states [2, 3]. Electrical measurements conducted at low temperatures on the vicinal SiC(001) samples demonstrate the opening of a transport gap in the nanostructured trilayer graphene up to 1.3 eV [4], which is induced by self-aligned periodic nanoboundaries. The transport gap opening produces high current on-off ratio of 10^4 [4, 5]. The magneto-resistance measurements disclose an exceptional big positive magneto-resistance in parallel magnetic field with strong temperature dependence [6]. It has been shown that graphene layer rippling near domain boundaries lead to one-dimensional conductivity (along the domain boundaries) at low temperatures and to accumulation of electrons with a particular spin direction at the boundaries. Moreover, nanodomain boundaries with ripples have the potential to work as a spin-filter and can result in a positive magnetoresistance at low temperature.

This work was supported by Beijing Institute of Technology Research Fund Program for Young Scholars, Science Foundation Ireland (SFI) (No. 12/IA/1264), Russian Foundation for Basic Research (Grant Nos. 17-02-01139, 17-02-01291), Marie Curie IIF grant within the 7th EC Framework Program.

1. O.V. Yazev and S.G. Louie, *Nature Mater.*, **9**, 806 (2010).
2. P. Ruffieux et al., *Nature*, **531**, 489 (2016).
3. K. Nakada et al., *Phys. Rev.*, **B 54**, 17954 (1996).
4. H.-C. Wu, A.N. Chaika, et al., *ACS Nano*, **9**, 8967 (2015).
5. A.N. Chaika, V.Yu. Aristov, O.V. Molodtsova, *Prog Mater Sci.*, **89**, 1 (2017).
6. H.-C. Wu, A.N. Chaika, et al., *Nature Commun.*, **8**, 14453 (2017).

9:20am **2D+EM+MI+NS-TuM-5 Discovering and Visualizing Ferromagnetism in Intrinsic Two Dimensional Materials**, *Jing Xia*, University of California Irvine

INVITED

In this talk, I will discuss our recent results on discovering and visualizing in 2D magnetism using a unique scanning Sagnac MOKE microscope, which is based on a Sagnac interferometer technique and has achieved unprecedented nano-radian level Kerr and Faraday sensitivity even at DC. In exfoliated Cr₂Ge₂Te₆ (CGT) atomic layers, we report the discovery of intrinsic ferromagnetism in 2D van der Waals crystals, defying the well-known Mermin-Wagner theorem. Unlike 3D magnetism, the ferromagnetic order in this 2D system is stabilized by magnetic anisotropy from the CGT structure, which is not present in graphene. As a result, changing the magnetic anisotropy with a small external magnetic field was found to strongly enhance the Curie temperature, which is a feature unique to 2D magnetism.

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11:00am **2D+EM+MI+NS-TuM-10 Onset of Buckling Folding and Slipping Instabilities in 2D Materials under Compressive Strain**, *Jaehyung Yu, E Ertekin, A van der Zande*, University of Illinois at Urbana-Champaign

Atomic membranes of monolayer 2D materials represent the ultimate limit in size of nanoelectromechanical systems. These materials have high mechanical strength, yet low bending modulus leading to high pliability. Adding in the diverse active electronic properties of different 2D materials, atomic membranes will allow new next generation technologies like highly strainable crumpled or folded electronics, or 3D origami devices based on 2D materials. In order to realize these new technologies it is important to understand how the rules of continuum membrane mechanics break down on the atomic scale and how these deformations will affect the electronic properties, including the role of compressive stress, bending, adhesion and interlayer shear.

Here, we present a combined experimental and theoretical study of the onset of instabilities such as buckling, folding and slip on the properties of 2D materials and heterostructures under compression. We generate periodic fold structures of the graphene, MoS₂, and their heterostructures by introducing the compressive stresses with the pre-strained stretchable substrate. We analyzed then measured the membrane morphology using atomic force microscopy (AFM) under increasing levels of uniaxial compression up to 30%. We observed that the strain-relaxation mechanism of atomic membranes could be varied from generating and growing standing folds to collapsing to generate triple folds based on the mechanical properties including 2D modulus, bending stiffness, adhesion and interlayer shear energies. The onset of these instabilities depends on the 2D material or heterostructure making up the membranes. In graphene folds grow then collapse at compressive strain of ~5%. In monolayer MoS₂ standing folds grow to a fixed height of ~20 nm but do not collapse. Instead, new folds are generated in between the existing folds.

We use density functional theory (DFT) to model the morphology of the same structures under compressive slack. We find that, in multi-layer 2D materials, the onset of slip between the layers is crucial parameters to decide the bending stiffness of the material. We found that the superlubricity between the layers allows the linear scaling of bending stiffness with the number of layers, which violates the conventional cubic scaling of bending stiffness in continuum mechanics.

We unite the atomic scale simulation with the experiment through a continuum model to compare the period, shape, and transition strains extract the variations in adhesion and bending energy of different 2D materials and heterostructures to find the deformation of 2D materials under the compressive strain.

11:20am **2D+EM+MI+NS-TuM-11 Title: Spatially-Resolved Contact-Free Electrical Characterization of Transition Metal Dichalcogenide Films Grown by Chemical Vapor Deposition.**, *Miguel Isarraraz, L Bartels*, University of California, Riverside

Surface Acoustical Waves (SAWs) and Transition Metal Dichalcogenides (TMDs), separately, are topics of current research due to their present and future use in telecommunications and beyond-CMOS technology. The interaction between a SAW and a 2D electron gas has been previously studied by measuring the absorption of the SAW by GaAs and, more recently, graphene [i,ii]. Here, the interaction between a SAW and a TMD is studied using MoS₂ directly grown by chemical vapor deposition on 128°YX-cut LiNbO₃. By focusing a 532 nm laser on the sample, the generation of electron-hole pairs is found to enhance the attenuation of the SAW as expected, and this technique can be used to spatially resolve variations inside triangular MoS₂ islands. Furthermore, the time dependence of the SAW attenuation with laser exposure is used to distinguish between heating and electronic effects. The induced acoustoelectric current, laser power, and SAW excitation power dependence are discussed. This technique provides a means of electrically characterizing atomically thin semiconducting film that avoids the limitations of metallic contacts.

[i] Weinreich, G., Acoustodynamic effects in semiconductors. *Phys. Rev.* **104**, 321 (1956); <http://dx.doi.org/10.1103/PhysRev.104.321>

[ii] Hoskins, M. J.; Morkoç, H.; and Hunsinger, B. J., Charge transport by surface acoustic waves in GaAs. *Appl. Phys. Lett.* **41**, 332 (1982); <https://doi.org/10.1063/1.93526>

[iii] Miseikis, V.; Cunningham, J. E.; Saeed, K.; O'Rourke, R.; and Davies, A. G., Acoustically induced current flow in graphene. *Appl. Phys. Lett.* **100**, 133105 (2012); <https://doi.org/10.1063/1.3697403>

11:40am **2D+EM+MI+NS-TuM-12 Electronic, Thermal, and Unconventional Applications of 2D Materials**, *Eric Pop, E Yalon, C McClellan, K Smithe, C English, M Mleczo, M Muñoz Rojo, N Wang, S Suryavanshi, I Datye, C Bailey, A Gabourie, M Chen, V Chen, K Schauble, R Grady*, Stanford University

INVITED

This talk will present recent highlights from our research on two-dimensional (2D) materials and devices including graphene, boron nitride (h-BN), 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. On the fundamental side, we have measured record velocity saturation in graphene [1,2], as well as the thermal properties of graphene nanoribbons [3]. These are important for electronic applications, which can exhibit substantial self-heating during operation [4]. Taking advantage of low *cross-plane* thermal conductance, we found unexpected applications of graphene as ultra-thin electrode to reduce power consumption in phase-change memory [5]. We have also demonstrated wafer-scale graphene systems for analog dot product computation [6].

We have grown monolayer 2D semiconductors by chemical vapor deposition over cm² scales, including MoS₂ with low device variability [7], WSe₂, MoSe₂ – and multilayer TMDs MoTe₂ and WTe₂ [8]. Importantly, ZrSe₂ and HfSe₂ have native high-K dielectrics ZrO₂ and HfO₂, which are of key technological relevance [9]. Improving the electrical contact resistance [10], we demonstrated 10 nm transistors using *monolayer* MoS₂, with the highest current reported to date (>400 μA/μm), approaching ballistic limits [11]. Using Raman thermometry, we uncovered low thermal boundary conductance (~15 MW/m²/K) between MoS₂ and SiO₂, which could limit heat dissipation in 2D electronics [12]. We are presently exploring unconventional applications including thermal transistors [13], which could enable nanoscale control of heat in “thermal circuits” analogous with electrical circuits. Overall, these studies reveal fundamental limits and new applications that could be achieved with 2D materials, taking advantage their unique properties.

References: [1] V. Dorgan, M.-H. Bae, E. Pop, *Appl. Phys. Lett.* **97**, 082112 (2010). [2] M. Yamoah, et al., *ACS Nano* **11**, 9914 (2017). [3] M.-H. Bae et al., *Nature Comm.* **4**, 1734 (2013). [4] S. Islam, et al., *IEEE Electron Device Lett.* **34**, 166 (2013). [5] A. Behnam et al., *Appl. Phys. Letters.* **107**, 123508 (2015). [6] N. Wang et al., *IEEE VLSI Tech. Symp.*, Jun 2016, Honolulu HI. [7] K. Smithe et al., *ACS Nano* **11**, 8456 (2017). [8] M. Mleczo et al., *ACS Nano* **10**, 7507 (2016). [9] M. Mleczo, E. Pop, et al., *Science Adv.* **3**, e1700481 (2017). [10] C. English et al., *Nano Lett.* **16**, 3824 (2016). [11] C. English et al., *IEEE Intl. Electron Devices Meeting (IEDM)*, Dec 2016. [12] E. Yalon, E. Pop, et al., *Nano Lett.* **17**, 3429 (2017). [13] A. Sood, E. Pop et al. *in press* (2018).

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

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

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

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

INVITED

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

One of the manufacturing challenges for the valence change memory (VCM) type of ReRAM has been the development of substoichiometric switching layer films. Physical vapor deposited (PVD) substoichiometric TaO_x films are an attractive option for a VCM switching layer because they are complementary-metal-oxide-silicon (CMOS) compatible and are

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deposited at low temperatures. However, control of the oxygen partial pressure to produce substoichiometric TaO_x films cannot be directly achieved through flow control because the oxygen consumption by the Ta target and chamber surfaces is nonlinear as the chamber transitions from metal to insulator conditions. The oxygen partial pressure can be controlled using a feedback system, though feedback-assisted deposition techniques are difficult to regulate, making them ill-suited to production. One alternative to a feedback system is to deposit a higher stoichiometry TaO_x film, deposited in a more stable flow-partial pressure chamber regime, and use annealing to drive Ta into the film to achieve the desired stoichiometry. Here, we compare switching layers fabricated using both techniques, and discuss the relative merits of each technique. The devices are manufactured in crossbar arrays to be testable by automatic probers, enabling the collection of large scale yield and performance data sets across process splits.

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

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

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

INVITED

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

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

INVITED

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

In this presentation, we will focus on hardware acceleration of large Fully Connected (FC) DNNs in phase change memory (PCM) devices [1]. PCM device conductance can be modulated between the fully crystalline, low conductance, state and the fully amorphous state by applying voltage pulses to gradually increase the crystalline volume. This characteristic is crucial for memory-based AI hardware acceleration because synaptic weights can then be encoded in an analog fashion and be updated gradually during training [2,3]. Vector matrix multiplication can then be done by applying voltage pulses at one end of a memory crossbar array and accumulating charge at the other end. By designing the analog memory unit cell with a pair of PCM devices as the more significant weights and another pair of memory devices as the less significant weights, we achieved

classification accuracies equivalent to a full software implementation for the MNIST handwritten digit recognition dataset [4]. The improved accuracy is a result of larger dynamic range, more accurate closed loop tuning of the more significant weights, better linearity and variation mitigation of the less significant weight update. We will discuss what this new design means for analog memory device requirements and how this generalizes to other deep learning problems.

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

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

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

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

INVITED

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

The metal oxide resistive switching memory (RRAM) [2] offers non-volatility, good scalability, and monolithic 3D integration, making it a good candidate as on-chip high-capacity main memory and storage in the N3XT system. Our experimentally calibrated studies show that a N3XT system with RRAM as digital storage and CNFET as logic devices could achieve 2-3 orders of magnitude improvement in energy efficiency (product of execution time and energy) in a wide range of applications (e.g. PageRank, deep neural network inference) compared to a conventional 2D system. Such 3D nano-system has also been experimentally demonstrated with RRAM, CNFET and CMOS monolithically integrated to perform in-situ ambient gas classification [3] and hyper-dimensional computing [4].

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

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

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

Onset of the second quantum revolution is marked by proliferation of quantum technologies. Still mostly in the laboratory R&D phase, but likely to emerge soon as a growing sector of general consumer technology, quantum devices require constant supply of novel functional quantum materials. The current paradigm of meticulous long-term studies to understand fundamental properties in detail and be able to model them ab initio is unlikely to disappear; however, the rapid growth of technology may require modification of classical approach by accelerated discovery process

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aided by machine learning, data mining, and ability to model, synthesize and test novel materials quickly. In this presentation we will discuss opportunities and current developments in select classes of quantum materials, like low-dimensional materials, strongly correlated systems and topological insulators, and the role NSF plays in this rapidly growing area.

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

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

2D Materials Focus Topic

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

2D Device Physics and Applications

Moderator: Roland Kawakami, The Ohio State University

2:20pm **2D+EM+MI+MN+NS-TuA-1 Spin Relaxation and Proximity Effect in WS₂/Graphene/Fluorographene Non-local Spin Valves**, *Adam Friedman*, Laboratory for Physical Sciences; *K McCreary, J Robinson, O van 't Erve, B Jonker*, US Naval Research Laboratory

The mechanisms leading to spin relaxation in graphene and its heterostructures continue to be debated. Control of the spin relaxation in graphene-based structures is necessary to achieve the envisioned utility of graphene in future spintronic devices beyond Moore's law. Proximity induced spin relaxation caused by contact to a high spin-orbit material, such as WS₂, offers a promising avenue to manipulate the spin lifetime [1]. We demonstrate the operation of WS₂/graphene/fluorographene non-local spin valves and extract the spin lifetimes for a range of carrier concentrations by Hanle effect measurements. Four-terminal charge transport measurements allow us to calculate the momentum relaxation time as a function of carrier concentration and compare it to the spin lifetime. These data show that the D'yakonov-Perel' mechanism is the dominant spin relaxation mechanism for WS₂/graphene/fluorographene devices, while, for reference graphene/fluorographene devices, linear scaling between the spin and momentum lifetimes points to spin-flip scattering during strong elastic scattering events where the scattering event is strongly coupled to the electron spin. We attribute the change in spin relaxation type in part with the inclusion of WS₂ as a substrate to proximity induced spin-orbit coupling due to the adjacent WS₂ layer, and we compare our data to the literature.

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

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

Two dimensional (2D) materials and their heterostructures hold great promises in various applications due to their unique properties and newly discovered physics. Especially, high exciton binding energy and emergence of charged excitons, *i.e.* trions, have shown that 2D semiconductors, such as transition metal dichalcogenides (TMDs), are promising candidates for new concept optoelectronics. Although lots of optoelectronic devices based on the van der Waals heterostructures of 2D materials, such as photodetectors, solar cells, and light emitting devices, have been demonstrated, development of novel optoelectronic devices is still required to fully utilize unique properties of 2D materials and enable multi-functions and versatile applications. Here we demonstrate 2D field-effect light emitting transistors (2D-FELET) consisting of monolayer WSe₂ (light-emitting channel layer) and graphene contacts (tunable carrier injection electrodes). We encapsulated monolayer WSe₂ with two pieces of hexagonal boron nitride and fabricated graphene contacts to two ends of WSe₂. To selectively inject different types of charge (electrons and holes) at two graphene contacts, two separate top gates on top of WSe₂-graphene overlap regions were fabricated. By independent modulation of two top gates, Schottky barrier heights for electrons and holes can be tuned, which enables the selective charge injections. When two top gates are oppositely biased, electrons can be injected from one end of WSe₂ channel and holes can be injected from the other end. These opposite charges are recombined at the middle of WSe₂ channel, leading to strong light emission. The performance of the 2D-FELETs is tunable by additional electrical field from back gate. Furthermore, the devices produced in this work can be used as polarity-tunable FETs and photodetectors, simultaneously, which are beneficial for further CMOS integration. Our study shows great potential of 2D-FELETs toward future optoelectronic applications, which request ultra-thinness, transparency, flexibility, high efficiency, multi-functions, and high integration.

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

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

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

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

We further demonstrate quantum devices build on MoS₂.

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2. Oostinga et al., Nat. Materials 7, 151 (2007)
3. Allen et al., Nat. Comm. 3, 934 (2012)
4. [<https://www.nature.com/articles/ncomms14552#auth-1>] et al., Nat. Comm. 8, 14552 (2017)
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4:20pm **2D+EM+MI+MN+NS-TuA-7 GaN Microdisk Light-emitting Diode Display Fabricated on Graphene**, *Youngbin Tchoe, K Chung, K Lee, M Song, J Park, H Kim, J Park, G Yi*, Seoul National University, Republic of Korea

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

Here, we report on the fabrication and EL characteristics of ultrathin and individually addressable GaN microdisk LED arrays grown on graphene dots for microdisplay applications. GaN microdisks were prepared by epitaxial lateral overgrowth on patterned graphene microdots on SiO₂/Si substrates using MOVPE. After preparing the GaN microdisk arrays, *p*-GaN and InGaN/GaN multiple quantum well, and *n*-GaN layers were heteroepitaxially grown on the surface of the GaN microdisks. Ultrathin layers composed of GaN microdisk LED arrays on graphene dot were prepared by coating a polyimide layer and lifting-off the entire layers from the substrate. Then, single-walled carbon nanotubes (SWCNTs)/Ni/Au and SWCNTs/Ti/Au multiple electrode lines were formed on the top and bottom surface of GaN microdisk arrays in an aligned manner and crossing each other. The electrical and optical characteristics of the individually addressable GaN microdisk array on graphene dots were investigated by measuring their *I-V* curves and EL characteristics at various bending conditions. We also confirmed that the ultrathin micro-LED display worked reliably under flexible conditions and continuous operation mode.

4:40pm **2D+EM+MI+MN+NS-TuA-8 Room Temperature Magnetron Sputtering and Laser Annealing of Ultrathin MoS₂ for Transistor Device Fabrication on Flexible Polymer Substrates**, *Benjamin Sirota*, University of North Texas; *N Glavin*, Air Force Research Laboratory; *C Arnold, A Voevodin*, University of North Texas

Pulsed magnetron sputtering and subsequent laser annealing provide technologically attractive scalable route for producing two-dimensional (2D) semiconducting grade MoS₂ materials directly on the surface of flexible polymer substrates. In this study the room temperature magnetron sputtering was used to deposit 10 nm thick, amorphous MoS₂ films on flexible PDMS as well as rigid SiO₂/Si substrates. This was followed by 248

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nm pulsed laser annealing to produce polycrystalline 2H-MoS₂ over large areas. Raman and XPS analysis confirmed that pulsed laser annealing with about 1 mJ/cm² energy density had induced film crystallization from amorphous to hexagonal, while preserving MoS₂ chemical composition, and avoiding formation of oxide phases or damage to the temperature-sensitive polymer surface. Electrical measurements confirmed an order of magnitude improvement in electrical conductivity of the laser annealed films as compared to amorphous MoS₂. Top-gated field effect transistor (FET) devices with laser annealed sputter grown MoS₂ were directly fabricated on PDMS surfaces. Oxygen substitution of sulfur in sputter deposited MoS₂ and polycrystallinity of the laser annealed 2H-MoS₂ films resulted in low mobility values when compared to mechanically exfoliated and chemical vapor deposition grown single-crystal 2D MoS₂. However, the described approach is intrinsically scalable and provides a direct growth route for the fabrication of 2D transition metal dichalcogenide semiconducting devices on the surface of flexible and stretchable polymers.

5:00pm **2D+EM+MI+MN+NS-TuA-9 Black Phosphorus: Fundamental Properties and Emerging Applications**, *Han Wang*, University of Southern California **INVITED**

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

5:40pm **2D+EM+MI+MN+NS-TuA-11 Patterned Growth of Hybrid Bulk-2D Tungsten Diselenide for Transistor Applications**, *Quinten Yurek, I Liao, D Barroso, A Nguyen, N Duong, G Stecklein, L Bartels*, University of California, Riverside

As device dimensions shrink, surfaces and interfaces between materials make up a larger volume fraction of a device leading to degrading device properties in 3D materials. One solution is to use 2D materials, however these materials introduce additional challenges. For instance, high resistance Schottky barriers and a small number of free charge carriers in comparison to bulk materials. The effective mobility of field effect transistors (FETs) based on two-dimensional (2D) single-layer transition metal dichalcogenide (TMD) films is frequently limited by barriers at the contacts, as opposed to the native properties of the TMD material. Specifically, high resistance Schottky barriers form at the TMD/metal interface because of the film's thinness and resulting small number of carriers. Here we demonstrate a scalable single-step deposition method for nanoscale hybrid 2D/3D TMD structures encoded by lithographic patterning prior to deposition. By confining the metal contact to the bulk regions of WSe₂, the effective mobility is increased to nearly 100 cm²V⁻¹s⁻¹ with an on/off ratio >10⁵ for bottom-gated devices (through 300nm of oxide), even for comparatively long channels (>5 microns) and absent other contact optimization. Our process involves lithographic patterning of a hafnium (IV) dioxide film onto the SiO₂/Si substrate prior to TMD growth. Bulk-like 3D WSe₂ is observed to grow at the location of the hafnia, while 2D single-layer material is grown in regions of bare SiO₂. Systematic evaluation of transport data allows us to extract Schottky barrier heights and other fundamental properties of our hybrid devices. We demonstrate that this process can be used to create devices with metal/3D TMD contacts, which exhibit a reduced Schottky barrier height, while continuing to use 2D TMD channels, which result in an excellent on-off ratio.

6:00pm **2D+EM+MI+MN+NS-TuA-12 Enhanced Ionic Sensitivity in Solution-Gated Graphene-Hexagonal Boron Nitride Heterostructure Field-Effect Transistors**, *A Radadia, Nowzesh Hasan, B Hou, A Moore*, Louisiana Tech University

The charge transport in solution-gated graphene devices is affected by the impurities and disorder of the underlying dielectric interface and its interaction with the solution. This paper reports advancement in field-effect ion sensing by fabricating a dielectric isomorph, hexagonal boron nitride between graphene and silicon dioxide of a solution-gated graphene field effect transistor. Ionic sensitivity of Dirac voltage as high as -198 mV/decade for K⁺ and -110 mV/decade for Ca²⁺ were recorded. Increased transconductance due to increased charge carrier mobility was accompanied with larger ionic sensitivity of the transconductance due to larger ionic sensitivity of the charge carrier mobility. These findings define a standard to construct future graphene devices for biosensing and bioelectronics applications.

**Electronic Materials and Photonics Division
Room 101A - Session EM+2D+AN+MI+MP+NS-TuA**

Solar/Energy Harvesting and Quantum Materials and Applications

Moderators: Yohannes Abate, Georgia State University, Nicholas Strandwitz, Lehigh University

2:20pm **EM+2D+AN+MI+MP+NS-TuA-1 Plasmonic Metasurface Electrodes for Excitonic Solar Cells**, *Deirdre O'Carroll*, Rutgers, the State University of New Jersey **INVITED**

Excitonic organic solar cell technologies, while not currently competitive with inorganic-semiconductor analogues, can exhibit very small device embodied energies (due to comparatively low temperature and low energy-use fabrication processes), which is of interest for minimizing overall device cost and energy-payback time. To improve energy conversion efficiency in thin-film excitonic organic solar cells, light management using nanophotonic structures is necessary. Here, our recent work on improving light trapping in deeply-subwavelength excitonic organic semiconductor films using plasmonic metasurfaces will be presented. Numerous exciton-metasurface interaction phenomena, such as absorption-induced scattering, exciton-plasmon coupling and morphology-dependent surface plasmon light-trapping are observed to give rise to improved light trapping at different regions of the solar spectrum. Additionally, an approach to achieve the theoretical limits to the efficiency of excitonic organic photovoltaics (~22%) will be proposed that involves control of radiative recombination rate, and optimization of both photoluminescence quantum efficiency and photon recycling in organic semiconductor thin-films.

3:00pm **EM+2D+AN+MI+MP+NS-TuA-3 Photoemission Electron Microscopy as a New Tool to Study the Electronic Properties of an Inhomogeneous Semiconductor for Photovoltaics**, *M Berg*, Sandia National Laboratories; *J Kephart, A Munshi, W Sampath*, Colorado State University; *Taisuke Ohta, C Chan*, Sandia National Laboratories

The energy positions of the valence and conduction electronic states with respect to the vacuum level are essential parameters to evaluate how the band gaps of semiconductors or Fermi-levels of metals line up with respect to each other. Such electronic structures of materials can be determined using photoemission spectroscopy (PES). PES measurements, however, remain challenging for inhomogeneous materials with nano- to micrometer lateral dimensions due to its mesoscopic probing area, typically no less than several microns. Photoemission electron microscopy (PEEM) is a cathode lens electron microscopy technique that combines photoemission imaging with spectroscopic modes of operation to provide PES spectra from areas less than one micron in size. Here, we present PEEM studies of the electronic structure of polycrystalline cadmium telluride (CdTe) thin films, a test case to examine the applicability of this new microscopic approach to photovoltaic materials. Post-deposition CdCl₂ treatment of CdTe is known to increase photovoltaic efficiency. However, the precise chemical, structural, and electronic changes that underpin this improvement are still debated. In this study, PEEM was used to spatially map the vacuum level and ionization energy of CdTe films, enabling the identification of electronic structure variations between grains and grain boundaries. *In vacuo* preparation and inert environment transfer of oxide-free CdTe surfaces isolated the separate effects of CdCl₂ treatment and ambient oxygen exposure. Qualitatively, grain boundaries displayed lower

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work function and downward band bending relative to grain interiors, but only after air exposure of CdCl₂-treated CdTe. This study highlights the importance of probing the spatially varying electronic structure, elucidating the concurrent impacts of processing steps (CdCl₂ treatment and oxygen exposure) to develop a comprehensive picture of local electronic structure in an inhomogeneous semiconductor.

The PEEM work was performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility (DE-AC04-94AL85000). M. B. & C. C. were supported by a U.S. DOE-EERE SunShot BRIDGE award (DE-FOA-0000654 CPS25859). T. O. was supported by the CINT user program and Sandia LDRD. 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-NA0003525. The views expressed in the article do not necessarily represent the views of the US DOE or the US Government.

3:20pm EM+2D+AN+MI+MP+NS-TuA-4 Modification of Bandgap for Lead-Free Double Perovskite Cs₂AgInCl₆ with Bi Doping, Hassan Siddique, University of Science and Technology of China; H Da, X Wang, University of Science and Technology of China, China; R Dai, Z Wang, University of Science and Technology of China; Z Ding, Z Zhang, University of Science and Technology of China, China

Lead halide perovskites have the excellent luminescent properties but exist some vital disadvantages such as instability and Pb toxicity. Lead-free double perovskites draw attention due to a possible candidate for environment-friendly materials. Direct bandgap lead-free halide of Cs₂AgInCl₆ is one of them. [1] In this work Bi doping Cs₂AgInCl₆ (CAIC) was successfully prepared. Bi dopant above 15% CAIC can restrict the parity forbidden transition responding to sub absorption peak around 600 nm.[2] On the other hand, the intensity of photoluminescence enhances with the increasing Bi dopant and touches the maximum around 30% doping, then gradually loses its intensity with further doping due to the mechanism of the concentration quenching at room temperature. Bi doping in CAIC can also modify the band gap. The absorption spectra indicate that the band gap reduces from 3.10eV without Bi doping to 2.68eV for Cs₂AgIn_{0.30}Bi_{0.70}Cl₆. PL decay life time reveals the good intrinsic excitonic feature with less defect trappers [3]. Average life time for Cs₂AgIn_{0.70}Bi_{0.30}Cl₆ is 490 ns which is least among all other Cs₂AgIn_(1-x)Bi_xCl₆ doping. Thermogravimetric analysis (TGA) result reveals thermal stability of Cs₂AgIn_{0.30}Bi_{0.70}Cl₆ for the high-temperature 506°C. The Bi doping can decrease the band gap, restrict defect states, enhance PL and improve stability; these good performances make Cs₂AgIn_(1-x)Bi_xCl₆ more suitable for optoelectronic properties.

4:20pm EM+2D+AN+MI+MP+NS-TuA-7 Optimized (Quantum) Photonics, Jelena Vuckovic, Stanford University INVITED

Photonics has numerous applications ranging from optical interconnects, classical and quantum computing, to sensing (such as LIDAR and AR), and imaging. However, the state of the art photonics is bulky, inefficient, sensitive to environment, lossy, and its performance is severely degraded in real-world environment as opposed to ideal laboratory conditions, which has prevented from using it in many practical applications. Therefore, it is clear that new approaches for implementing photonics are crucial.

We have recently developed a computational approach to inverse-design photonics based on desired performance, with fabrication constraints and structure robustness incorporated in design process [1,2]. Our approach performs physics guided search through the full parameter space until the optimal solution is reached. Resulting device designs are non-intuitive (see Figure), but are fabricable using standard techniques, resistant to temperature variations of hundreds of degrees, typical fabrication errors, and they outperform state of the art counterparts by many orders of magnitude in footprint, efficiency and stability. This is completely different from conventional approach to design photonics, which is almost always performed by brute-force or intuition-guided tuning of a few parameters of known structures, until satisfactory performance is achieved, and which almost always leads to sub-optimal designs.

Apart from integrated photonics, our approach is also applicable to any other optical and quantum optical devices and systems. In recent years, color centers in diamond and silicon carbide (SiC) have emerged as a possible platform for implementation of quantum circuits [3,4]. We demonstrate how such quantum hardware can also be optimized to be robust, efficient, and scalable.

References

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5:00pm EM+2D+AN+MI+MP+NS-TuA-9 Optical Properties of Single Silicon Vacancies in 4H-SiC, H Banks, National Research Council Postdoc residing at the Naval Research Laboratory; O Soykal, Sotera Defense Solutions, Inc, residing at the Naval Research Laboratory; S Pavunny, R Myers-Ward, D Gaskill, Samuel Carter, U.S. Naval Research Laboratory

Defects in wide bandgap materials have generated substantial interest as promising systems for quantum information and quantum sensing due to bright, stable optical emission that is often coupled to long-lived spin states. One promising defect system is the silicon monovacancy in SiC (V_{Si}), which has a spin-3/2 ground state that can be optically polarized and maintain long spin coherence times even at room temperature. SiC is an attractive material in terms of mature growth and fabrication technology and also has a low natural abundance of nuclear spins, which reduces spin dephasing. While significant work has been performed to study the spin properties of V_{Si} for ensembles and even single defects, the optical properties and their connection to the spin system are less developed. Here we report on high resolution optical spectroscopy of single V_{Si} defects, specifically V2 defects, at low temperatures. Using laser excitation spectroscopy, the zero phonon line (ZPL) transitions corresponding to the m_s=±1/2 and m_s=±3/2 spin states are resolved, with a linewidth down to 70 MHz and a splitting of 1 GHz. While there is significant variation in the transition energies from one defect to another, the splitting of these lines is very uniform. We also find that emission from the V2 defect under resonant excitation of these lines rapidly decays on two very different timescales. Slow decay on a 10 ms timescale is attributed to photoionization of V_{Si} and can be prevented by periodically exciting the defect with a second laser at 745 nm. Fast decay on a μs or shorter time scale occurs due to a combination of intersystem crossing and spin polarization of the ground state. A significant difference in the decay rates of the two transitions is observed, which gives rise to spin-dependent photoluminescence intensity and non-resonant optical spin polarization. These results further our understanding of the connection between the optical and spin properties of this defect system that are necessary to optically control and readout the spin system as well as to develop a spin-photon quantum interface.

5:20pm EM+2D+AN+MI+MP+NS-TuA-10 Photoluminescence Studies on Patterned Silicon Vacancy Defects in Li Ion Implanted 4H-SiC for Scalable Quantum Device Applications, Shojan Pavunny, U. S. Naval Research Laboratory; S Carter, H Banks, R Myers-Ward, P Klein, U.S. Naval Research Laboratory; E Bielejec, Sandia National Laboratories; M DeJarld, A Bracker, E Glaser, D Gaskill, U.S. Naval Research Laboratory

Recently, silicon vacancy defect centers (V_{Si}) in the CMOS compatible wide bandgap semiconductor SiC hexagonal polytypes have drawn great research interest for future applications in scalable quantum information and quantum sensing mainly due to their high electronic spin (S = 3/2) with a long coherence time at room temperature. Realization of future densely integrated quantum devices will greatly benefit from the ability to deterministically induce the desired V_{Si} density at the optimal location in the three-dimensional solid-state matrix with nanometer accuracy and excellent optical properties. With this motivation, we demonstrate targeted formation of arrays of V_{Si} ensembles as well as single defects in high-quality 4H-SiC epilayers by a direct, maskless focused ion beam implantation technique with a designed lateral separation of ~5 μm and a ~25 nm spot size. We have carried out high-resolution optical spectroscopy studies (E_{Lc} and E_{||c}) on these arrays, in which lithium ions are implanted at doses varying from 10¹² – 10¹⁵ Li/cm² at a fixed energy of 100 keV to a depth of ~400 nm from the surface. Photoluminescence intensity and defect conversion yield with dose, photostability, fluorescence saturation, and V₁:V_{1'} intensity evolutions with temperature and excitation power were investigated. Results obtained from temperature dependent photoluminescence studies can provide key insights in the design and fabrication of scalable and reproducible three dimensional SiC quantum hybrid devices including photonic crystal cavities.

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5:40pm **EM+2D+AN+MI+MP+NS-TuA-11 Processing of Cavities in SiC Material for Quantum Technologies, Rachael Myers-Ward, K Hobart, K Daniels, A Giles, M Tadjer, L Luna, F Kub, S Pavunny, S Carter, H Banks, E Glaser, U.S. Naval Research Laboratory; P Klein, Sotera Defense Solutions; K Qiao, Y Kim, J Kim, Massachusetts Institute of Technology; K Gaskill, U.S. Naval Research Laboratory**

Silicon carbide is a material of interest for quantum computing and sensing applications owing to deep point defect centers with long spin coherence times (which characterizes the lifetime of the qubit), specifically the V_{Si} [1], divacancies [2] and nitrogen-vacancy centers [3]. These spin qubits have been isolated and coherently controlled, where V_{Si} have T_2 coherence times up to 100 μs [4] and divacancies to 1 ms [2], making these two defects of most interest to date. While the current spin coherence times have been shown to be as long as 1 ms, further improvements are needed to fully realize the potential of SiC for quantum applications. In this work, we create V_{Si} in epitaxial SiC and investigate fabricating the layers into microstructures suitable for using the V_{Si} photoluminescence (PL) emission. We have found 4H-SiC epitaxial layers grown under standard growth conditions and with varying doping densities from 10^{14} to 10^{18} cm^{-3} have no measurable V_{Si} present, as determined by confocal PL. To introduce V_{Si} , we used 2 MeV electron irradiation in doses ranging from 0.75 to 75 kGy. This results in V_{Si} PL ranging from single to ensemble emission within the confocal volume. Hence, we are able to tune the vacancy concentration.

In order to improve the indistinguishable photons from the V_{Si} and/or divacancies for real applications, photonic crystal cavities (PCC) are used to tune the emission energy [4]. Our PCC design consists of a planar array of cylindrical holes approximately 220 nm wide in a slab of SiC, ~300-500 nm thin having an area $50 \times 50 \mu m^2$, similar to [4]. To maximize the PCC quality factor, the slab should have a large index of refraction difference on the top and bottom; i.e., an air gap is desired under the slab. To achieve this goal, we have identified four fabrication methods to create the PCC. One of these techniques is to use remote epitaxy as an innovative approach which entails growing epitaxial graphene on a SiC substrate by means of Si sublimation. Silicon carbide is then grown on a monolayer of graphene to the desired film thickness [5]. This thin SiC layer is then transferred, facilitated by the weak van der Waal forces at the graphene/SiC substrate interface, to a substrate more amenable to cavity fabrication. All four fabrication methods will be presented in detail.

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6:00pm **EM+2D+AN+MI+MP+NS-TuA-12 Investigation of Localized Electronic structures of PbSe Quantum Dot Superlattice on a Highly Oriented Pyrolytic Graphite (HOPG), Il Jo Kwak, S Ueda, University of California at San Diego; A Abelson, C Qian, M Law, University of California, Irvine; A Kummel, University of California at San Diego**

Lead-Chalcogenide quantum dots are of interest due to the facility of adjustment of their electrical and optical properties. Using a colloidal self-assembly technique, extended arrays of nanocrystal QDs superlattices can be generated. The quantum confinement within individual QDs in the superlattice is relaxed and delocalization of wave functions occurs due to coupling of the QDs. In the QD solids, bulk-like electronic bands with a bandwidth of 100~200 meV are expected to form which yield much higher carrier mobility and diffusion length compared to weakly-coupled QDs; however, the electronic properties of such highly ordered QD arrays are not fully understood. The local density of state of a highly ordered monolayer PdSe superlattice was investigated by low temperature scanning tunneling microscopy.

A monolayer of PbSe QDs was prepared using the Langmuir Schaefer deposition technique. First, oleate-capped PbSe QDs dispersed in hexane were drop casted onto diethylene glycol surface. After the hexane was evaporated, a (111) in-plane oriented polycrystalline FCC superlattice was formed on the diethylene glycol surface. NH_4SCN solution was applied onto the oleate-capped PbSe superlattice film. The injection of NH_4SCN initiates the ligand exchange and phase transformation from an FCC to a simple cubic structure superlattice. A monolayer QD superlattice was prepared on a HOPG substrate. Afterward, the HOPG sample was loaded into a commercial UHV scanning tunneling microscopy chamber with a base

pressure of 1×10^{-10} torr. The sample was annealed to remove hydrocarbons and ligands from the surface. The topography of the QDs was observed with a tungsten tip. The STM images were acquired in constant current mode.

STM imaging showed the PbSe QD monolayer had 4-fold symmetry with an average inter QD spacing of 7nm. It is also found the height fluctuation of the QDs was 1nm indicating size variation of the QDs and imperfect crystal structure of the superlattice. Scanning tunneling spectroscopy was performed to investigate the electronic structure of the PdSe QDs using a variable z-mode with an external lock-in amplifier in the bias range of -2 to 2V. Single site STS showed resonant peaks from molecular orbitals of QDs before the ligand exchange process; however, the peaks were not observed after the ligand exchange due to necking between the QDs in the superlattice. In addition, the size of band gap was decreased as increasing the number of nearest neighboring QDs due to necking between QDs. Layer 2 QDs showed more p-type behavior than layer 1 QDs possibly due to the band bending effect at the interface of HOPG and QD superlattice.

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

SPM – Probing and Manipulating Nanoscale Structures

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

2:20pm **NS+AM+MI+MN+SS+TR-TuA-1 Building Artificial Quantum Matter with Dopant Atoms, Sven Rogge, University of New South Wales, Australia INVITED**

Atomic-scale engineering reached the level of control where single-atom devices can be reproducibly fabricated with high yield. This talk focuses on the progress of single dopant atom placement in the context of engineered quantum matter. Silicon offers a particularly interesting platform for single dopants because when isotopically purified it acts as a “semiconductor vacuum” for spins. This leads to extraordinary coherence that is used to realise donor atom based qubits. Spatially resolved tunnelling experiments reveal the spectrum and quantum state image of single atoms and tunnel coupled arrangements of atoms. These measurements grant access to the wavefunction of donors in the silicon lattice that makes it possible to pinpoint the dopants to their exact position in the lattice that is essential in the evaluation of engineered quantum matter. A first step towards engineered Hamiltonians for Fermionic systems in the form of atomic chains was taken where interacting dopants were employed to simulate a two-site Hubbard Hamiltonian at low effective temperatures with single-site resolution. Quasi-particle tunnelling maps of spin-resolved states with atomic resolution reveal interference processes from which the entanglement entropy and Hubbard interactions are quantified. We will present dopant based multi-electrode devices fabricated by the scanning probe hydrogen depassivation and decoration technique where the quantum state of the device can be manipulated and imaged in situ. The aim of this work is to build a two dimensional array of up to 30 spins in the solid state to implement complex highly correlated systems.

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

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

Different surfaces were investigated for their role in the surface-activated coupling reaction. Intact monomer molecules were found to self-assemble through hydrogen and halide interactions on Ag(100), resulting in well-packed molecular islands which impacted the organometallic structure ultimately formed after reaction. On Au(100), two competing intermediate dimers were observed resulting from a chiral covalent bond between base DBPQ molecules. Cis dimers were found to result in reaction products that

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became stuck as tetramers without the potential for further polymerization. Utilization of increasing coverage and a new surface identity that arose from the leaving Bromide resulted in selective formation of longer conjugated polymer chains composed of trans dimers. This study characterizes the ability of initial self-assembly and leaving groups to steer reaction dynamics and control the structure of a nanocarbon catalyst.

3:20pm **NS+AM+MI+MN+SS+TR-TuA-4 Detecting the Tip Shape Dependence of the Plasmonic Photon Emission under STM**, *Songbin Cui*, Pohang University of Science and Technology, Republic of Korea; *U Ham*, Institute for Basic Science (IBS), Republic of Korea; *T Kim*, Pohang University of Science and Technology, Republic of Korea

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

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4:20pm **NS+AM+MI+MN+SS+TR-TuA-7 Advances in SPM Methods for Energy-relevant Materials**, *Marina Leite*, University of Maryland College Park

INVITED

The scientific understanding of nanoscale materials and devices is continuously growing ever since atomic force microscopy (AFM) has enabled us to image these systems at similar length scale. Specifically, there is a pressing need for functional imaging as energy-relevant technologies are becoming dominated by nano- and mesoscale constructs. In this presentation I will review my group's recent research discoveries based on new AFM methods to measure and determine how the electrical, chemical, and/or optical properties influence overall photovoltaic device behavior [1,2]. We realize novel functional imaging AFM-based methods to elucidate the driving forces for the dynamic response of the perovskites upon and post-illumination [3], and polycrystalline materials for solar cells [4,5]. We map nanoscale variations in open-circuit voltage $V_{oc} > 300$ mV under 1-sun illumination, not revealed by conventional AFM tools. Using fast-KPFM (16 seconds/scan) while maintaining high spatial sensitivity, we map, in real-time, the dynamics of the V_{oc} in perovskite solar cells with spatial resolution < 100 nm. Unexpectedly, we identify a 'residual V_{oc} ' post-illumination, attributed here to iodine ion migration, a process that takes place in a time scale of several minutes. We foresee our functional imaging tool to be implemented in the identification of stable perovskite compounds, ranging from lead-free and non-toxic alternatives to new options for tandem designs.

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

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

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

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

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

5:00pm **NS+AM+MI+MN+SS+TR-TuA-9 Coherent Electrical Contact to Semiconducting Graphene Nanoribbon**, *Chuanxu Ma*, *L Liang*, Oak Ridge National Laboratory; *Z Xiao*, North Carolina State University; *A Puzetky*, *K Hong*, Oak Ridge National Laboratory; *W Lu*, *J Bernholc*, North Carolina State University; *A Li*, Oak Ridge National Laboratory

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

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

5:20pm **NS+AM+MI+MN+SS+TR-TuA-10 Visualizing Coordination Structures of Small Gas Molecules to Metallo-porphyrin on Au(111) Using Scanning Tunneling Microscopy**, *MinHui Chang*, Korea University, Republic of Korea; *Y Chang*, *N Kim*, Korea Advanced Institute of Science and Technology (KAIST); *U Jeon*, *H Kim*, Korea University, Republic of Korea; *Y Kim*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea; *S Kahng*, Korea University, Republic of Korea

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

5:40pm **NS+AM+MI+MN+SS+TR-TuA-11 Effects of Dimensionality on the Reactivity of Carboxylic-Acid-Terminated Monolayers**, *Dominic Goronzy*¹, *E Avery*, *N Gallup*, University of California, Los Angeles; *J Staněk*, *J Macháček*, *T Baše*, Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic; *K Houk*, Chemistry and Biochemistry, University of California, Los Angeles; *P Weiss*, University of California at Los Angeles

Self-assembled monolayers (SAMs) are an advantageous construct to modify surfaces and thereby to tune material properties. Three major determinants affect the spontaneous assembly of monolayers: the substrate-monolayer interface, the interactions between the adsorbate molecules, and the monolayer-environment interface. By controlling the exposed functional groups in the SAM, this interface between the surface and the environment can be probed and manipulated. To examine how exposed carboxyl functional groups modulate the properties of SAMs, we have tethered thiol-functionalized carborane cage molecules with and without a carboxyl group to Au{111} surfaces. Using scanning tunneling microscopy (STM), visualization of the *para*-functionalized carboxylic acid carboranethiol was only possible in the form of a mixed monolayer of functionalized and unfunctionalized molecules. These experiments demonstrated that the functionalized molecule adopted the same nearest-

¹ NSTD Student Award Finalist

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neighbor spacings on the surface as the unfunctionalized *para*-carboranethiol, approximately 7.2 Å. By comparison, in our study of carboranethiols with a carboxylic acid functional group attached in the *meta* position, we have been able to image pure functionalized monolayers *via* STM with these molecules showing nearest-neighbor spacings of 8.4 Å, approximately 1 Å larger than the unfunctionalized carboranethiols. Studies of two different isomers of *meta*-carboranethiolate carboxylic acids yielded similar results. In order to examine the effects of changing dimensionality from a 3D solvent system to a 2D thin film, we applied contact angle titration to probe the reactivity of the carboxylic acid head group. These experiments demonstrated a substantial shift from a pK_a of 3–3.2 in solution (3D) to an apparent surface pK_a of approximately 6.5–7.5. Density functional theory calculations were performed to test the effects of desolvation by 2D confinement and showed shifts in pK_a consistent with the experimental data. Together, these results support the concept that the confinement in a 2D environment induces significant changes in reactivity in the molecules, as evidenced by the pK_a shift. Thus, precise positioning of functional groups in SAMs is an important tool to investigate the behavior of surface-confined molecules. This system may also serve as a model to explore dimensionality effects in biological systems, including proteins confined within membranes.

Surface Science Division

Room 203C - Session SS+HC+MI-TuA

Oxides/Chalcogenides: Structures and Reactions

Moderator: Andrew Teplakov, University of Delaware

2:20pm SS+HC+MI-TuA-1 New Eyes for Nanocatalysis: Atomic Scale Investigations of TiO₂ Chemistry, *Melissa Hines*, Cornell University INVITED

The atomic-scale surface chemistry of nanocatalysis has remained relatively unexplored for two simple reasons. First, nanocatalysts are too small to be studied individually with most surface science techniques. Second, nanocatalysts are typically used at ambient pressure or in solution — conditions where surface contamination is a significant concern. In this talk, I will review our work in developing “new eyes for nanocatalysts” that address both issues.

Addressing the issue of size, I will show that hydrothermal crystal growth techniques can produce anatase nanocrystals suitable for study at the atomic-scale with STM and a panoply of techniques. Despite being synthesized in solution, the nanocrystal surfaces are very clean and passivated by a protecting monolayer. Using these crystals, I will show that the most commonly used functionalization chemistry for oxide nanocatalysts, a carboxylic acid solution, causes the spontaneous reorganization of the nanocatalyst, leading to a five-fold increase in the number of reactive sites.

Addressing the issue of contamination, I will explain the chemical origin of the molecularly ordered interfaces that have been observed by researchers around the world when TiO₂ surfaces are exposed to air or solution. Although these structures have recently been attributed to a new (2 × 1) ordered state of adsorbed H₂O, we show that clean TiO₂ surfaces selectively adsorb atmospheric organic acids that are typically present in parts-per-billion concentrations while effectively repelling other adsorbates, such as alcohols, present in much higher concentrations. This finding may have important implications for TiO₂ photocatalysis, as the self-assembled carboxylate monolayer resists desorption under environmental conditions while effectively blocking the transition metal sites typically implicated in photocatalysis.

As time allows, I will also show that solution-phase techniques can be used to prepare a wide variety near-atomically-perfect, self-assembled monolayers on TiO₂ surfaces.

3:00pm SS+HC+MI-TuA-3 Coverage-dependent Water Agglomerates on Fe₃O₄ Surfaces, *Zdenek Jakub*, Vienna University of Technology, Austria; *M Meier*, University of Vienna, Austria; *J Hulva*, *J Pavelec*, *M Setvin*, *M Schmid*, *U Diebold*, Vienna University of Technology, Austria; *C Franchini*, University of Vienna, Austria; *G Parkinson*, Vienna University of Technology, Austria

The interaction between iron oxides and water plays a key role in many natural and technological processes. Recent water adsorption studies have found significant complexity on metal oxides, with reports of mixed-mode adsorption and hydrogen bonding. Here we present a multi-technique study of water adsorption on Fe₃O₄ surfaces. Utilizing quantitative temperature programmed desorption (TPD) and X-ray Photoelectron Spectroscopy (XPS), we identify four partially dissociated phases in the

submonolayer regime on the Fe₃O₄(001), corresponding to coverages of 9, 8, 6 and 3 molecules per surface unit cell. These are investigated by non-contact atomic force microscopy (nc-AFM) with tip functionalized by CO molecule, and the observed structures are further interpreted by DFT-based calculations. We clearly demonstrate the existence of partially dissociated dimers and trimers at lower coverage, and a build-up of complex hydrogen-bonded network with increasing coverage. Applying the same approach on the Fe₃O₄(111) we discuss the general trends of water adsorption on Fe₃O₄ surfaces.

3:20pm SS+HC+MI-TuA-4 Reversible Structural Evolution and Identification of the Catalytically Active Phase of NiCoO_xH_y During the Oxygen Evolution Reaction (OER), *Bruce E. Koel*, Princeton University

Significant improvements in the activity of transition metal oxides (TMOs) for the oxygen evolution reaction (OER) have been made by tailoring the morphology and crystal structure of the catalysts, incorporating dopants, and using conductive supports. However, the complex composition and structure of TMO catalysts have hindered the elucidation of clear structure-activity correlations. We have utilized a range of electrochemical techniques, such as electrical impedance spectroscopy (EIS), and spectroscopic techniques, including ambient pressure photoelectron spectroscopy (APPEs), for characterization of pure and Ni-modified cobalt (oxy)hydroxide electrocatalysts for OER. In particular, operando Raman spectroscopy and electrochemical techniques were used during the oxygen evolution reaction to identify the composition and local structure of electrodeposited CoO_xH_y and NiCoO_xH_y catalyst films. In these studies, several unique initial catalyst structures and crystallinities were prepared by subjecting the samples to a variety of thermal and electrochemical conditioning procedures before evaluation. During oxygen evolution, Ni-modified CoO_xH_y films with lower initial crystallinity underwent substantial structural evolution that began with an irreversible transformation of a spinel local structure to an amorphous CoO structure at low anodic potentials. Increasing anodic polarization with elevated oxygen evolution rates caused additional structural conversion of the amorphous CoO structure to a complex phase that can be described as an amalgamation of NiOOH and layered CoO₂ motifs (NiOOH-h-CoO₂). The formation of this active structure was correlated with improved OER activity. Formation during oxygen evolution of the same NiOOH-h-CoO₂ structure independent of the initial cobalt oxide structure suggests that this active phase identified in these studies could be the universally active structure for NiCoO_xH_y catalysts.

4:20pm SS+HC+MI-TuA-7 Understanding the Growth and Chemical Activity of Titania-Supported MoS_x Clusters, *Donna Chen*, University of South Carolina; *R Galhenage*, University of California at Irvine; *H Yan*, University of Louisiana Lafayette; *D Le*, *T Rawal*, *T Rahman*, University of Central Florida

MoS_x clusters have been grown on TiO₂(110) in order to provide a model surface for better understanding adsorbate interactions and chemical activity of supported MoS_x clusters; MoS₂ particles have exhibited excellent catalytic activity for a variety of reactions, particularly for hydrodesulfurization and photocatalysis, and interactions with the support are believed to induce new electronic properties. The MoS_x clusters were grown by deposition of Mo on titania in an atmosphere of H₂S, followed by annealing to 950 K in H₂S. Scanning tunneling microscopy experiments show that clusters with elongated, rectangular shapes and flat tops are formed, and the long axes of the clusters have specific orientations with respect to the [001] direction on TiO₂(110). In contrast, deposition of Mo in the absence of H₂S results in a high density of smaller, round clusters that cover the majority of the surface. The morphologies of MoS_x clusters do not change after exposure to various gases (D₂, CO, O₂, methanol) in ultrahigh vacuum. However, exposure to higher pressures of O₂ (250 mTorr) or air causes the clusters to disintegrate as Mo in the clusters becomes oxidized. Temperature programmed desorption studies with CO on the MoS_x clusters show a distinct desorption peak at 275 K, which is not observed on metallic Mo or titania. Density functional theory calculations demonstrate that the presence of the titania support changes in the favored adsorption site for CO from the (-1010) edge in the pristine MoS₂ to the (10-10) edge for the supported MoS₂. Furthermore, the MoS_x/TiO₂(110) interfacial sites are not favored for CO adsorption.

*This work is partially supported by DOE grant DE-FG02-07ER15842.

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4:40pm **SS+HC+MI-TuA-8 Analyzing Single Atom Catalysts using Low Energy Ion Scattering (LEIS), Thomas Grehl**, IONTOF GmbH, Germany; *R ter Veen*, Tascon GmbH, Germany; *D Kunwar*, A Datye, University of New Mexico; *H Brongersma*, IONTOF GmbH and Tascon GmbH, Germany

An important goal of heterogeneous catalyst synthesis is the dispersion of the active metal uniformly on a catalyst support, ideally achieving atomic dispersion. Isolated atoms dispersed on oxide supports (single-atom catalysts) provide efficient utilization of scarce platinum group metals, and higher reactivity as well as better selectivity for a range of catalytic reactions.

One of the challenges is to achieve high enough loadings and to prevent agglomeration by limiting the synthesis and operation temperature. Consequently, the characterization of these materials is essential to monitor the dispersion.

Low Energy Ion Scattering (LEIS) is a surface analytical technique that quantitatively determines the elemental composition of the outer atoms with ultimate surface sensitivity. LEIS is compatible with non-conducting supports and insensitive to topography, making it an ideal tool to analyze both model and industrial catalysts. Due to its unique surface sensitivity the results of the analysis usually correlate directly with the properties of the catalyst.

This contribution demonstrates the analysis of Pt/CeO₂ single atom catalysts using LEIS. During synthesis (atom trapping) the Pt precursor is heated in air at 800 C to form mobile Pt species that deposit on the support and are strongly bound. On high surface area ceria, metal loadings of 3 wt. % can be achieved while maintaining almost exclusively single atoms. We will describe how LEIS was essential to demonstrating the single atom nature of the catalyst. In conjunction with X-ray absorption spectroscopy (XAS), Aberration-Corrected Scanning TEM (AC-STEM) and Diffuse Reflectance Infrared Absorption Spectroscopy (DRIFTS) we were able to develop an accurate picture of the sites that bind Pt ions on the support. The atomistic model for the single atom Pt catalyst was corroborated by Density Functional Theory (DFT).

The LEIS results revealed that with increasing metal loading, the fraction of Pt visible to LEIS decreased by 20%. However XAS, DRIFTS and AC-STEM confirmed that the Pt was present in single atom form even at the highest metal loadings. Further analysis led to the realization that the Pt atoms are present in close proximity at high loadings, causing some of the Pt to be rendered invisible to LEIS. The loss in LEIS signal could be correlated with the differences in reactivity for CO oxidation, which otherwise could not be easily explained. This application demonstrates the extreme sensitivity of LEIS which makes this analytical approach essential for study of heterogeneous catalysts used in industry.

Part of this work was supported by DOE grant DE-FG02-05ER15712 and NSF grant EEC-1647722.

5:00pm **SS+HC+MI-TuA-9 Synthesis and Characterization of Metals Supported on ZnO Nanoparticles, Amanda Haines, D Ferrah, J Hemminger**, University of California at Irvine

Various metals on transition metal oxide supports, such as Cu/ZnO, have been widely studied to understand their role in CO₂ hydrogenation. However, there still remains a dispute as to the role of the oxide supports and the surface oxidation state of the active metal and its efficacy in the reduction of CO₂, namely on the nature of CO₂ adsorption and activation. Here, we have designed and characterized a model catalytic system that will enable us to explore the chemistry of various metals (M: i=Pt,Cu) on ZnO supports. ZnO nanoparticles (NPs) have been deposited on an inert highly oriented pyrolytic graphite (HOPG) substrate by physical vapor deposition (PVD). From scanning electron microscopy (SEM), we have seen that hexagonal shaped ZnO nanoparticles are formed on a defect-free HOPG substrate. Different surface plasma treatments have been explored to create defect sites on the HOPG substrate to better control the density of the ZnO NPs and various substrate temperatures have been studied to investigate its effect on the size, morphology, structure and chemistry of the NP growth process. Different metals, Pt and Cu, are photodeposited on the ZnO NPs and fully characterized using X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and temperature programmed desorption (TPD) to gain fundamental information about the oxidation states and active sites of these M_i/ZnO NPs. Future work will involve reactivity studies on the fully characterized M_i/ZnO NPs using ambient pressure X-Ray photoelectron spectroscopy (AP-XPS) to investigate the surface chemistry, intermediates and products of this catalyst to gain insight into the reaction mechanism of CO₂ hydrogenation.

5:20pm **SS+HC+MI-TuA-10 Molecular Water Adsorption and Reactions on α -Al₂O₃(0001) and α -Alumina Particles, Greg Kimmel, N Petrik**, Pacific Northwest National Laboratory; *P Huestis*, J LaVerne, University of Notre Dame; *A Aleksandrov*, T Orlando, Georgia Institute of Technology

Alumina and its interactions with water are important in areas ranging from electronics and catalysis to environmental science. However, a basic understanding of the adsorption and reactions of water on even the simplest alumina surface, the (0001) surface of α -alumina, remains elusive. We have investigated the adsorption and reaction of water on single crystal, α -Al₂O₃(0001) in ultrahigh vacuum, and α -alumina particles in ambient conditions, using temperature programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), and other surface science techniques. For a water coverages of 1 and 2 H₂O/(surface Al³⁺) on α -Al₂O₃(0001), no evidence for the surface hydroxyls expected from dissociative adsorption was observed, while the ν_2 vibration of molecular water was observed. Electron-stimulated desorption of molecular water at low coverages also indicated molecular or mixed (molecular plus dissociative) adsorption. In contrast with the single crystal results, IR spectra of water adsorption on alumina particles indicated the presence of surface hydroxyls that persist even after annealing to high temperatures in oxygen. The results, which are consistent with at most a small amount of water dissociation on the Al-terminated (0001) surface, are difficult to reconcile with calculations suggesting that the barrier to dissociation is small. However, the results are consistent with recent vibrational sum frequency experiments showing that the hydroxylation of the Al-terminated (0001) surface takes many days even at ambient pressures and temperatures.

5:40pm **SS+HC+MI-TuA-11 Applying Low Temperature Titration for Determination of Metallic Sites on Active Oxide Supported Catalysts, Jerry Pui Ho Li, Z Liu, Y Yang**, ShanghaiTech University, China

Catalysts are used in a variety of applications from the production of fuels or consumer chemicals, and the environment. Characterization of such catalysts is critical, since it allows for an accurate representation of its effectiveness. For optimum design and efficient utilization of catalysts, it is important to be able to connect model catalyst and industrial catalyst turnover frequencies (TOF) based on the same benchmark for active sites, such as metallic sites, for catalyst evaluation and further kinetics studies. Characterization of the active sites with chemisorption is ideally performed with high time resolution and sensitivity; particularly for catalysts with low loading of the active particles.

Chemisorption study is the common method for active site determination, but has limitations for active heterogeneous catalysts; particularly industrial catalysts because the method often cannot distinguish the redox on metallic sites and catalyst support. An online micro reactor combined with online mass spectroscopy was developed for kinetics studies within wide temperature (as low as liquid nitrogen) and pressure ranges. Pt and Cu based catalysts are used as demonstration of this technique for metallic sites quantitative calibration in this study. Pt catalysts were characterized using CO oxidation and Cu catalysts were characterized using N₂O decomposition. By comparing titration products curves (CO₂ for Pt catalysts, and N₂ for Cu catalysts) versus temperature for both supported samples, narrow subzero temperature windows are found for each catalyst, demonstrating that the titration products are only related with metallic sites. Pure metallic powder was analyzed for confirmation. Specialized chemisorption procedure was established for each sample. This procedure shows a reliable direct titration measurement recipe for the characterization of supported catalysts, quantifying only the metallic sites for catalysts while being selective against surfaces that contribute secondary reactions often found with more complex supports.

We also present a specialized chemisorption technique applied for metallic sites determination of Au nanoparticles on TiO₂ support through CO at low temperature by comparing IR assignment.

6:00pm **SS+HC+MI-TuA-12 Giant Optical Anisotropy in Hexagonal Perovskite Chalcogenides with Quasi-1D Structures, Shanyuan Niu**, University of Southern California; *G Joe*, University of Wisconsin - Madison; *H Zhao*, M Mecklenburg, University of Southern California; *T Tiwald*, J.A. Woollam Co. Inc; *K Mahalingam*, Air Force Research Laboratory; *H Wang*, University of Southern California; *M Kats*, University of Wisconsin - Madison; *J Ravichandran*, University of Southern California

Optical anisotropy is a crucial building block to engineer the polarization of light in polarizing optics, light modulators, imaging and communication systems. While metamaterial architectures with form birefringence can overcome the limited optical anisotropy available in widely used natural

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anisotropic crystals, their deployment is limited by the demanding fabrication. We demonstrate the realization of giant optical anisotropy via chemically engineering the polarizability tensor in a natural material, BaTiS₃, which has a highly anisotropic quasi-1D structure and features easily accessible in-plane anisotropy. Large single crystals were grown with the chemical vapor transport method. We report the observation of a large, broadband infrared birefringence and linear dichroism. As-grown crystals demonstrate strong dichroism with two distinct optical absorption edges for light with polarizations along two principal axes. To our knowledge, the unprecedented birefringence in the transparent region is more than twice as large as that in any other bulk crystal.

Actinides and Rare Earths Focus Topic

Room 202C - Session AC+MI+SA-WeM

Magnetism, Complexity, and Superconductivity in the Actinides and Rare Earths

Moderators: Melissa Denecke, University of Manchester, UK, David Geeson, AWE, James Tobin, UW Oshkosh

8:00am AC+MI+SA-WeM-1 Strong electron-electron Interactions in the Actinides: Using Organometallics to Probe Delocalization Effects, *Corwin Booth*, Lawrence Berkeley National Laboratory **INVITED**

Systems exhibiting strong electron-electron interactions remain at the forefront of inquiry into complex properties of condensed matter systems due to their exciting properties (eg. superconductivity) and their resistance to being understood on a fundamental level. A bottleneck toward a better understanding has been the difficulty of the required many-body calculations for extended solids. Alternatively, calculations on small molecules require fewer and better approximations, potentially offering a better description. Although strong electron-electron interactions are well established in extended solids, recent work on lanthanide organometallic coordination compounds has demonstrated the importance of such interactions, fueled by the propensity for certain 4f orbitals to be partially delocalized. Meanwhile, recent work on the actinides challenges the canonical view that the 5f electrons can bond in the light actinides but are essentially localized in the heavier actinides. A major stumbling block for such work is the paucity of known structures for elements beyond Am in the periodic table.

For the discussion presented here, work on Ce and Yb organometallics will provide context in terms of f-occupancy and in bonding characteristics and the effect on magnetism. The role of strongly electron interactions will be described in terms of configuration interaction (CI) and related calculations.

Occupancy is measured using Ln L_{II}-edge x-ray absorption near-edge structure (XANES) techniques, and local structure (EXAFS) measurements demonstrate the final effect on the bonding at the metal center. Of particular interest is what happens in formally Ce(IV) systems that exhibit strong interactions.

XANES measurements of actinides are more difficult to interpret and will be discussed. The focus will be, however, on EXAFS measurements across the An series in the presence of strongly oxidizing ligands. Chosen ligands include hydroxypyridonone (HOPO), with less oxidizing ligands, such as diethylenetriaminepentaacetic acid (DTPA) used for comparison. Cations include Th, U, Pu, Am, Cm, Bk, and Cf. Discussions will center on nearest-neighbor bond lengths, using DFT calculations as a guide. The surprising role of covalency in the late actinides will be considered, both in terms of the EXAFS results and in terms of the edge shifts.

This work was supported by the U.S. Department of Energy (DOE), Office of Science (OS), Office of Basic Energy Sciences (OBES), under Contract No. DE-AC02-05CH1123.

8:40am AC+MI+SA-WeM-3 Structure and Magnetism of U-based Thin Films and Heterostructures, *Evgeniya Tereshina-Chitrova*, Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic; *L Havela*, Charles University, Prague, Czech Republic; *T Gouder*, Z Bao, Institute for Transuranium Elements, Germany; *M Dopita*, Charles University, Prague, Czech Republic; *R Caciuffo*, Institute for Transuranium Elements, Germany **INVITED**

Uranium is the basic component of most nuclear fuels. The production of uranium-based films has advantage over bulk materials studies as it allows performing advanced physics and chemistry experiments on small amounts of radioactive material and on its clean and smooth surfaces. Other interesting field is uranium magnetism. Although uranium itself is non-magnetic, uranium compounds display a rich variety of magnetic phenomena intimately related to the variable character of the 5f electron states [1]. Additional degrees of freedom can be used in thin films, in which the reduced dimensionality and structure modifications far exceed the limits imposed by thermodynamics, obeyed in bulk systems. We review the achievements in the field of sputter-deposited films, in which variations of deposition conditions can dramatically suppress crystallinity of the deposited material. The 5f itinerant magnetic systems (as US or UN [2]) react to the low substrate temperatures and high deposition rates by decreasing ordering temperatures and eventually by the loss of U magnetic moments. The strong ferromagnetism of uranium hydride is, on the other hand, almost insensitive, which underlines its local-moment character.

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The possibility to combine films of various materials on the nanostructure scale can also give rise to new functionalities. For example, the exchange bias (EB) effect [3], arising as a result of combination of a ferromagnet biased by exchange interaction at the interface to an antiferromagnet, is particularly interesting if uranium magnetism are involved. The new ingredient, strong spin-orbit interaction, can lead to very strong magnetic anisotropy, which represents an essential parameter. We have been systematically studying films of Fe₃O₄ (ferromagnet) grown using different substrates on the top UO₂, playing the role of biasing antiferromagnet [4]. The resulting high bias field (> 0.2 T) and a proximity effect, in which the high Curie temperature of Fe₃O₄ provides the EB functionality even at temperatures exceeding ordering of UO₂, demonstrate the promising aspects of using actinides in this non-traditional way.

The work is supported by the Czech Science Foundation under the project #18-02344S. Part of the work was supported by "Nano-materials Centre for Advanced Applications," Project No.CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF.

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9:20am AC+MI+SA-WeM-5 Field Induced Lifshitz Transitions in URu₂Si₂, *E Calegari*, Univ Federale Santa Maria, Brazil; *S Magalhaes*, Universidade Federale Rio Grande do Sul, Brazil; *Peter Riseborough*, Temple University **INVITED**

We report calculations on an unusual phase of the Under-screened Anderson Lattice (UAL) model, the so called spin-dependent inter-orbital density wave that has been proposed as describing the "Hidden Order" (HO) phase of URu₂Si₂.

We determine the effects of an applied magnetic field. Since the order parameter describes an ordering in the x-y plane, the electronic properties of the system are anisotropic below the critical temperature THO. We show that the magnetic susceptibility becomes anisotropic below THO.

Furthermore, for fields applied along a spontaneously chosen hard axis, THO decreases towards zero and that the HO transition changes from second order to first order at a large value of the magnetic field. Also, we find that the system undergoes a cascade of field-induced Lifshitz transitions and also show how these properties originate from the dependence of the quasi-particle bands on the orientation of the applied field. The good qualitative agreement with experimental findings provides strong support for the proposed description of the HO phase as a spin-dependent inter-orbital density wave phase.

11:00am AC+MI+SA-WeM-10 New Form of Uranium Hydride - *UH₂*, *Ladislav Havela*, *M Paukov*, *M Dopita*, *L Horak*, *P Minarik*, *M Divis*, *I Turek*, Charles University, Prague, Czech Republic; *D Legut*, VSB-Technical University of Ostrava, Czech Republic; *T Gouder*, *A Seibert*, *F Huber*, European Commission - Joint Research Centre; *E Tereshina-Chitrova*, Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic

Most of f-elements form with hydrogen both di- and trihydrides. Actinide and rare-earth dihydrides occur, as a rule, in the CaF₂ structure type. Uranium represents an exception, only UH₃ is present in the binary phase diagram. It exists in two different structure types. The metastable form α-UH₃ forms in the Cr₃Si structure type, which is in fact bcc U lattice filled with hydrogen. The stable form β-UH₃ has a larger cubic cell with two different U sites. Both forms are ferromagnets with the total U moment of ≈ 1 μ_B/U and the Curie temperature T_c ≈ 165 K. We have recently synthesized UH₃ thin films using a reactive sputter deposition. XRD analysis indicated the β-UH₃ structure, modified by a pronounced (001) texture and compressive residual strains imposed by the deposition dynamics. Magnetization measurements proved T_c = 165 K.

The sputter deposition on a cooled substrate (T = 170 K) using Si wafer the crystal structure turned different. The deposited material is undoubtedly cubic, of the fcc type, and the lattice parameter a = 5.3598 ± 0.0014 Å is very close to that of PuH₂ (a = 5.359 Å) and NpH_{2+x} (a = 5.343-5.355 Å). Hence we can assume that UH₂ in the fluorite structure was formed. The key role in stabilization plays likely the effect of substrate (Si has a = 5.431 Å) in combination with low temperature deposition. The UH₂ film was subsequently subjected to magnetization measurements, which indicated a ferromagnetic ground state with T_c ≈ 125 K. This is lower than in the UH₃ phases, although the U-U spacing in UH₂ should be higher, 3.78

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Å, than in both UH₃ phases (3.31 and 3.60 Å for β- and α-UH₃, respectively). This fact points to the U-U interaction being more important than the U-U spacing. The ferromagnetic state is also the ground state obtained from ab-initio calculations. Scalar relativistic calculations (LDA) for experimental lattice parameter yield the spin moment $\mu_s = 2.0 \mu_B/U$. LDA+U (U = 2.25 eV) gives the equilibrium lattice parameter $a = 539.9 \text{ \AA}$, i.e. 0.7% larger than the experimental one, the ferromagnetic ground state with (111) easy-magnetization direction and the magnetic anisotropy energy $E_a = 9 \text{ meV}$. The total moment $0.45 \mu_B/U$ consists of 2.59 μ_B and -3.04 μ_B .

This work was supported by the Czech Science Foundation under the grant No. 18-02344S. The work at JRC Karlsruhe was supported by the European FP7 TALISMAN project, under contract with the European Commission. Part of the work was supported by the project "Nanomaterials centre for advanced applications", Project No. CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF.

11:20am AC+MI+SA-WeM-11 Tuning of Electronic Properties of U- and RE-Metallic Systems by H Absorption, *Silvie Maskova*, Charles University, Prague, Czech Republic; *K Miliyanchuk*, Ivan Franko National University of Lviv, Lviv, Ukraine; *A Kolomiets*, Lviv Polytechnic National University, Lviv, Ukraine; *L Havela*, Charles University, Prague, Czech Republic

The sensitivity of the interactions in the intermetallic systems to modification of the crystal structure makes the experimental techniques involving alteration of the atomic arrangement especially important. Various studies under compression are well-known examples of such methods. From this point of view hydrogenation can be treated as a complementary technique that provides „negative“ pressure. Hydrides can be defined as compounds for which the hydrogen absorption leads to the modifications of the crystal structure, such as pure lattice expansion or the formation of a new structure. As a result, the new compounds (hydrides) exhibit qualitatively new physical properties and such modifications provide us with additional information on the peculiarities of interatomic interactions in the initial compounds.

As an example, we will compare the impact of H absorption on U- and RE-compounds using A₂T₂X (A = Rare-Earth (RE) or actinide, T = transition metal, X = p-metal) compounds crystallizing in the tetragonal Mo₂FeB₂ structure type (space group *P4/mmm*). U₂T₂X interact with H₂ only at high pressure ($\approx 100 \text{ bar}$) reaching 2 H/f.u. The H absorption produces a lattice expansion (lower than 10 %), while the tetragonal structure is preserved. Higher H concentrations, which can be achieved in some RE₂T₂X compounds (up to 8 H atoms/f.u.), lead to amorphization or structure symmetry changes (with volume expansion exceeding 20 %), imposed by a minimum H-H distance requirement.

Magnetic properties of U-compounds strongly depend on the U-U distances. Hydrogen intrusion modifies the lattice by expanding it without changing the crystal-structure type leading to a 5f band narrowing. As a consequence, doping of U intermetallics by interstitial hydrogen leads to stronger magnetic properties. On the other hand, the hydrogen absorption has opposite effect on magnetic properties of RE₂T₂X compounds. For RE compounds, hydrogenation affects mainly the inter-site exchange interaction, which is weakened presumably by reducing the concentration of conduction electrons, responsible for the RKKY interaction.

11:40am AC+MI+SA-WeM-12 Magnetic Structures of U_nRhIn_{3n-2} Materials, *Attila Bartha*, *M Klicpera*, Charles University, Prague, Czech Republic; *P Cermak*, Forschungszentrum Juelich GmbH, Germany; *B Ouladiaz*, Institute Laue-Langevin, France; *J Custers*, Charles University, Prague, Czech Republic
In the past decade, U-compounds crystallizing in the HoCoGa₅-type structure (*P4/mmm*), frequently referred to as 115, have been in the focus of attention in experimental and theoretical research. Vigorous activities have been motivated by the high superconducting transition temperature of $T_c = 8.7 \text{ K}$ in PuRhGa₅ [1] and $T_c = 18.5 \text{ K}$ in PuCoGa₅ [2]. No further superconductivity has been reported in neither U-115 nor in the closely related U₂TGa₈ compounds (T = transition metal). However, interesting magnetic properties have been observed: neutron scattering experiments revealed that UNiGa₅ exhibits the G-type antiferromagnetic (AFM) phase, while UPdGa₅ and UPtGa₅ exhibit the A-type AFM state. Note that G-type indicates a 3D Néel state, while A-type refers to a layered AF structure where spins align FM in the *ab* plane and AFM along the *c* axis [3]. The difference in the two magnetic structures is significant since it implies a sign change of the nearest-neighbor (NN) interaction.

Here we report on the magnetic structures of URhIn₅ and U₂RhIn₈, two new members of the U_nT_mX_{3n-2m} (X=In,Ga) family of compounds [4]. URhIn₅ displays AFM order below $T_N = 98 \text{ K}$. The observed increase of the resistivity for current parallel [100], [110] and [001] are reminiscent to a spin-density

wave (SDW) type of transition with the gap opening first along the [001] direction [5]. U₂RhIn₈ enters the AFM state at $T_N = 117 \text{ K}$. No increase in resistivity in the vicinity of T_N is found which would hint to a SDW gap opening. Neutron diffraction experiments on URhIn₅ were performed at the Heinz Maier-Leibnitz Zentrum (MLZ) in Garching using the triple axis spectrometer PANDA. Single crystals with accumulated mass of 10mg where glued on an Al-plate. Our results confirmed the magnetic propagation vector $k=(1/2,1/2,1/2)$ predicted by NMR experiments [6] and a magnetic moment of $1.65 \mu_B/U^{3+}$. The neutron study on U₂RhIn₈ has been conducted at ILL, Grenoble using D10 on only one single crystal with $m \approx 1 \text{ mg}$. Analysis revealed a propagation vector $k=(1/2,1/2,0)$ and an ordered moment of $1.7 \mu_B/U^{3+}$. UIn₃, URhIn₅ and U₂RhIn₈ all show G-type AFM phase. While the *c*-axis parameter differs significantly the *a* lattice parameter equals 4.601Å, 4.621Å and 4.6056Å respectively, being a change of less than 1% pointing to the fact that the NN coupling is important for the type of magnetic structure.

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12:00pm AC+MI+SA-WeM-13 Insights into the Magnetic Dead Layer in La_{0.7}Sr_{0.3}MnO₃ Thin Films from Temperature, Magnetic Field and Thickness Dependence of their Magnetization, *Navid Mottaghi*, *M Seehra*, *R Trappen*, *S Kumari*, *C Huang*, *S Yousefi*, *G Cabrera*, *A Romero*, *M Holcomb*, West Virginia University

Detailed dc magnetization (*M*) measurements of a 7.6 nm La_{0.7}Sr_{0.3}MnO₃ thin film samples is investigated. The sample was fabricated by pulsed laser deposition. Zero-field-cooled (ZFC) *M* vs. applied field (*H*) cooled down to $T = 5 \text{ K}$ reveal the presence of negative remanent magnetization (NRM) as well as in ZFC *M* vs. temperature (*T*) measurements in $H = 50 \text{ Oe}$ and 100 Oe . ZFC and FC (field-cooled) protocols are used to determine the blocking temperature T_B in different *H*. Isothermal hysteresis loops at different *T* are used to determine the temperature dependence of saturation magnetization (M_s), remanence (M_R) and coercivity H_c . The M_s vs. *T* data are fit to the Bloch law, $M_s(T) = M_0(1 - BT^{3/2})$, showing a good fit for $T < 100 \text{ K}$ and yielding the nearest-neighbor exchange constant $J/k_B \approx 18 \text{ K}$. The variations of T_B vs. *H* and H_c vs. *T* are well described by the model often used for randomly oriented magnetic nanoparticles with magnetic domain diameter $\approx 9 \text{ nm}$ present in the dead-layer of thickness $d = 1.4 \text{ nm}$. Finally, the data available from literature on the thickness (*D*) variation of Curie temperature (T_c) and M_s of LSMO films grown under 200, 150, and 0.38 mTorr pressures of O₂ are analyzed in terms of the finite-size scaling, with M_s vs. *D* data fit to $M_s(D) = M_s(b)(1-d/D)$ yielding the dead layer thickness $d = 1.1 \text{ nm}$, 1.4 nm and 2.4 nm respectively.

Electronic Materials and Photonics Division Room 101A - Session EM+AN+MI+SS-WeM

Surface and Interface Challenges in Electronics and Photonics

Moderators: Andy Antonelli, Nanometrics, Michael Filler, Georgia Institute of Technology

8:00am EM+AN+MI+SS-WeM-1 Few Monolayer Atomic Layer Deposition (ALD) to Engineer New Surfaces and Interfaces, *Parag Banerjee*, Washington University in St. Louis
INVITED

Atomically precise modification of surfaces and interfaces with few monolayer material leads to improved understanding and significant enhancements in properties, performance and reliability of heterogeneous materials and devices. This talk highlights the impact of few monolayer insulators, wide bandgap semiconductors and metals, deposited using atomic layer deposition (ALD) on a variety of surfaces and interfaces with direct relevance to electronic and photonic devices.

The first part of this talk deep dives into the process science of ALD in its early cycles. The nature and structure of few monolayer ALD films is highlighted. In particular, configurational state and entropy of adlayers during every half-cycle of ALD¹ is exploited to exquisitely manipulate nucleation and growth of metallic Ru thin films.²

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In the second part of this talk, applied aspects of few monolayer engineering of surfaces and interfaces is discussed. Case studies included are the non-linear optical phenomena on Au-Al₂O₃ and Au-ZnO surfaces,³ high performance photocatalysts for CO₂ photoreduction,⁴ improved optoelectronic responses from surface passivated CuO nanowires⁵ and few monolayer Ta₂O₅ to improve reliability of electrochromic windows.⁶

Regardless of the application, ALD at its ultimate thickness limit holds true potential for surface and interface engineering. The control of this process appears to be remarkably simple and yet, has hidden complexities that continue to push the boundaries of discovery of new materials and concept devices.

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8:40am **EM+AN+MI+SS-WeM-3 Lattice-alignment mechanism of SiGe on Sapphire**, *HyunJung Kim*, National Institute of Aerospace; *S Choi*, NASA Langley Research Center

In the conventional heteroepitaxy processes, the deposition of dissimilar materials has been made with the same or similar crystal structure and perfect or nearly matching lattice constants, such as Ge/Si (diamond cubic), InAs/GaAs (zinc-blende), and GaN/Al₂O₃ (hexagonal/trigonal). On the other hand, the super-heteroepitaxy of two semiconductors with dissimilar crystal structures such as SiGe (diamond cubic)/Al₂O₃ (trigonal) is not readily achievable but requires scrupulous manipulation of growth conditions for single crystal formation. Epitaxial growth patterns of SiGe on *r*-plane and *c*-plane of sapphire substrates show 90°-rotated and 60°-rotated twin defects, respectively [1,2].

A team at NASA Langley Research Center developed a technique for super-hetero-epitaxy of single crystal SiGe growth; diamond-cubic structure of SiGe on trigonal structure of the *c*-plane sapphire substrate by a transformed lattice structure under a new lattice-alignment model [2]. Although the growth conditions were effective for the formation of single crystal film, how the mechanism or physics of single crystal formation of SiGe at the interface of sapphire was not theoretically and experimentally defined with the order of atomic scale level in arrangement. This work presents the interfacial image of SiGe/Al₂O₃ using high-resolution transmission electron microscope (HRTEM) to show the SiGe/Al₂O₃ interfacial bonding for superheteroepitaxy mechanism. The first two atomic layers of the SiGe are Si-rich where Si atoms match with the surface oxygen lattice of the Al₂O₃ substrate. After the Ge composition increases, the monolayer spacing is also increased due largely to the dominance of Ge composition since the lattice constant of Ge is bigger than that of Si. These results highlight the importance of a cleanliness of sapphire substrate, the Si-affinity to oxygen that ties up Si- of SiGe with the oxygen of sapphire, and eventually causing the deformation of SiGe cubic structure for super-heteroepitaxy [3]. From the essential understanding of the SiGe/Al₂O₃ interface mechanism, both low temperature SiGe super-heteroepitaxy and the III-V or II-VI semiconductor epitaxy are possible.

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9:00am **EM+AN+MI+SS-WeM-4 An Effort to Resolve Band Offset Anomalies in ZnO/GaN Heterostructures**, *Monu Mishra¹*, A Gundimedda, V Vandana, G Gupta, CSIR-National Physical Laboratory, India

Gallium Nitride (GaN) and Zinc Oxide (ZnO) are well established wide band gap (WBG) semiconductors facilitating potential application in futuristic energy-efficient opto/micro-electronics technology. Despite of owing the merits of both semiconductors, the understanding of ZnO/GaN heterostructures is still posing challenges. The available reports display anomalies amongst calculated valence band offset (VBO) and defect state of ZnO/GaN interface. The influence of surface and interfacial properties perturbs the electronic structure, localized charge density and defect states at the interface, yet the impact of these properties on VBO requires more scientific attention. Hence, sharp interfaces of ZnO/GaN heterostructures (ZnO thickness = 2, 5 and 8 nm) were fabricated via atomic layer deposition (ALD) of ZnO on MOCVD grown highly crystalline GaN epilayer and further investigated by HR-XPS, UPS and PL spectroscopy. The impact of ZnO thickness on band bending (upwards & downwards), surface/interface dipole strength and defects states (vacancies, interstitials, donor/acceptors etc.) on valence & conduction band offsets (VBO/CBO) were thoroughly analysed. It was observed that the VBO at the interface was reduced via 0.6 eV as the ZnO thickness was increased from 2 nm to 8 nm which was ascribed to interface dipole strength along with dramatic change in localized BB (downwards-flatband-upwards). A type-II band alignment was perceived at all ZnO/GaN interfaces though the nature & contribution of defects states (especially oxygen vacancies and zinc interstitials) varied incommensurately. The defect band spectra revealed a blue shift (~502 eV) which correspond to the conversion of yellow-green emission in ultrathin ZnO/GaN heterostructure (2 nm ZnO) to characteristic green emission in bulk ZnO. The analysis revealed that the thickness of ZnO overlayer in ZnO/GaN heterostructure significantly alters the electronic structure and defect states at the interface and thus the resolution of anomalies in the present analysis would be useful for the fabrication of ZnO/GaN heterostructure based efficient optoelectronic devices.

9:20am **EM+AN+MI+SS-WeM-5 Stress Relaxation in the Si-SiO₂ System and its Influence on the Interface Properties**, *Daniel Kropman*, T Laas, Tallinn University, Estonia; *A Medvids*, Riga Technical University, Latvia

It is known that internal mechanical stresses (IMS) due to the differences in the thermal expansion coefficients between films and substrates and lattice mismatch appear in the Si-SiO₂ system during the process of its formation and that point defects (PD) generation and redistribution could be used to reduce partially the surface stress. However, this process on the atomic scale is till not studied. The goal of the present report is to investigate the stress relaxation mechanism in the Si-SiO₂ system using EPR, IR absorption spectroscopy, scanning elektron microscopy (SEM) and samples deflection measurements. PD density and stresses in the Si-SiO₂ system were varied by oxidation condition (temperature, time, cooling rate, ambient) and by Si₃N₄ deposition on SiO₂. Different sign of the thermal expansion coefficient of the SiO₂ and Si₃N₄ on Si allow to modify the IMS at the interface. It has been found that samples deflection decreases or increases simultaneously with EPR signal intensity depending on the oxidation condition (temperature).

At oxidation temperature 1100°C the deflection of the samples(h) decreases with the increase of EPR signal intensity (vacancies), while at a oxidation temperature 1200°C EPR signal (I) and deflection increase simultaneously. Those allows to suggest that at lower oxidation temperature PD (vacancies) reduce the tensile IMS in Si, while at higher oxidation temperature compressive IMS created PD in SiO₂ (E' centers). At an intermediate oxidation temperature tensile stresses in Si and compressive stresses in SiO₂ may be equal and compensate each others. It has been found that at oxidation temperature 1130°C IMS at the Si-SiO₂ interface are lower than at 1100°C and 1200°C. Lower defect density on samples crosssection microphotos obtained by SEM and PD density diminishing in samples oxidized at 1130°C confirmed this suggestion. In Fig.2 the EPR signal and IR absorption line-width dependence on the oxidation time is shown. It can be seen, that EPR signal and IR absorption line-width at 1100 cm⁻¹ dependence on the oxidation time (oxide thickness) is nonmonotonous and depended on the cooling rate. In slowly cooled samples the increase of the EPR signal is accompanied by the decrease of Δv but, in fast cooled samples EPR signal and Δv increase simultaneously with increase oxidation time.

Absent of the cooling rate influence on the PD density and Δv dependence on the oxidation time at I(t) and Δv(t) dependence intersection points

¹ National Student Award Finalist

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show, that IMS by an appropriate choice of the SiO₂ film thickness dissipate.

9:40am EM+AN+MI+SS-WeM-6 Unique Sensitivity to Deep Trap States Demonstrated by CREM of Broad Bandgap Dielectric Layers, Hagai Cohen, Weizmann Institute of Science, Israel; K Steirer, Colorado School of Mines

Chemically resolved electrical measurements (CREM) present an efficient and sensitive means for studies of structural-electrical inter-relationships in heterostructures. Operated in-situ to x-ray photoelectron spectroscopy (XPS), the technique is yet far from being fully exploited. Recent progress in our CREM instrumentation has, however, opened new opportunities to which this report is dedicated. Using broad-bandgap dielectric layers, such as SiO₂, SiON and ZnOS, we tested the CREM resolving power and sensitivity to charge trap states. These experiments yielded band diagrams with fine details on charge traps, which typically require the application of advanced optical techniques combined with the electrical characterization tools.

In addition, an intriguing process of doubly triggered conductance in ZnOS was observed. The ZnOS layers exhibited very poor conductance under either electrical or optical input signals, whereas simultaneous application of the two yielded extremely high sample currents. Based on the in-situ derived band diagram, a comprehensive explanation of the effect is provided. Moreover, we show how the CREM analytical tool can also provide a potential activator of future related devices.

11:00am EM+AN+MI+SS-WeM-10 Fabrication of Multilayered Optically Active Nanocrystal Solids by Surface Passivation using Metal Oxides: ALD vs CVD, Riya Bose, A Dangerfield, University of Texas at Dallas; S Rudolph, University of Texas; Y Chabal, A Malko, University of Texas at Dallas

Semiconductor nanocrystal quantum dots (NQDs) provide a powerful platform for optoelectronic applications with their size/shape/composition tunable properties and inexpensive solution based synthesis techniques. Integration into solid state devices requires deposition of NQD films, and often a controlled assembly of multilayered NQD structures to ensure maximum light absorption and optimum efficiency of the devices. However, thin film fabrication is found to degrade its properties compared to NQDs in solution, especially a decrease in the photoluminescence (PL) quantum yield (QY) is frequently observed. Also, the bottleneck for fabrication of multilayer NQD films remains the use of solution phase deposition methods, where the solvent in the subsequent step of deposition dissolves the initial layer until each NQD layer is rendered insoluble by means of any surface passivation technique. Surface passivation techniques also play a critical role to protect the deposited layers from oxidation and deterioration. An attractive method to passivate NQD films during the deposition as well as from environmental exposure is to overcoat them with various metal oxides grown using atomic layer deposition (ALD). Though there are few reports of ALD encapsulation of NQD films, they mostly attend to charge transfer-based devices and aim to improve carrier mobilities. Typically, such studies report a significant quenching of the PL intensity after encapsulation. In this study, we aim to investigate the exact growth mechanism of metal oxide layers by ALD on the surface of NQD films and how it, along with the ALD parameters, affects their PL properties. With the aid of in-situ FTIR and ex-situ XPS measurements during Al₂O₃ deposition on oleic acid capped CdSe-ZnS core-shell nanocrystals, it is observed that the interaction of the metal precursor trimethyl aluminium (TMA) with the surface of the NQDs leads to the reorganization of the ligands as well as replaces Zn, leading to PL intensity quenching. In order to prevent this, we opted for a pulsed chemical vapour deposition (CVD) like approach for metal oxide deposition where simultaneous purging of both the metal and oxygen precursors leads to formation of metal oxide in a gas phase in the immediate vicinity of the NQD surface. We found that minimization of TMA interaction with the NQDs' surface indeed leads to enhancement of the PL intensity and elongation of carrier PL lifetime. These measurements provide clear indication of defect-free surface passivation proving that CVD-like Al₂O₃ encapsulation is a suitable technique for controlled deposition of multilayered NQD structures that preserves its optoelectronic properties.

11:20am EM+AN+MI+SS-WeM-11 The Role of Surface Oxides for the Optoelectronic Performance of III-V Semiconductor Nanowires, J Colvin, A Troian, O Persson, A Mikkelsen, Rainer Timm, Lund University, Sweden

III-V semiconductor nanowires (NWs) have a large technological potential within electronics, optoelectronics, and energy harvesting [1,2], mainly due to their flexibility in creating heterostructures by axial stacking during epitaxial growth. Because of their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly

determined by surface properties. We have previously studied surfaces and surface oxides of semiconductor NWs by scanning tunneling microscopy and spectroscopy (STM/S) [3] as well as X-ray photoemission spectroscopy [4]. Here, we will correlate the surface properties of InAs and InP NW heterostructures with their electrical and photovoltaic behavior, which has been measured for individual upright-standing NWs using the STM tip as local nanoprobe [5].

InP and GaInP pin-junction NWs have been cleaned from their native oxide by annealing under atomic hydrogen background and re-oxidized by exposure to ambient conditions. By illuminating the InP NWs that were contacted by the STM nanoprobe, we observed a decrease of the open-circuit voltage from 0.75 V to 0.70 V upon native oxide removal and an increase back to 0.76 V upon re-oxidation, confirming the need of surface passivation for improving InP solar cells. However, the ideality factor of the NW pin-diodes remained constant at $n = 1.82$ upon oxide removal, but improved to $n = 1.67$ upon re-oxidation. Furthermore, our XPS results indicate the outdiffusion of Zn dopants from the p-doped NW segments, forming a Zn-rich shell around the NW.

A more significant effect of the presence of native surface oxide was found for InAs NWs which consist of one segment of wurtzite and one segment of zincblende crystal structure. Upon removal of the native surface oxide, we obtained an increase in conductivity of these NWs by two orders of magnitude, while reference NWs with pure wurtzite structure showed a slight decrease in conductivity with the same surface treatment. This effect can be explained by a staggered type-II surface band alignment at the wurtzite/zincblende interface of oxidized NWs, which turned into flat-band conditions upon oxide removal, as confirmed by nano-focus XPS measurements.

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11:40am EM+AN+MI+SS-WeM-12 Photonic Annealing of 2D Transition Metal Dichalcogenides for Tailored Optical Properties, Rachel Rai, K Gliebe, University of Dayton; Air Force Research Laboratory; N Glavin, R Kim, A Jawaid, R Wheeler, L Bissell, Air Force Research Laboratory; C Muratore, University of Dayton

Thin layers of transition metal dichalcogenides (TMD) have attracted significant interest in the field of optoelectronics due to their unique light absorption and emission properties in the visible frequency range. Development of bright, flexible, large area emission sources based on 2D materials using photonic annealing represents an exciting opportunity for future quantum systems. Here we introduce new correlations relating the optical properties of WSe₂, a well-known single photon emitter, to post-processing annealing techniques to include lasers, broadband radiation, and nanoscale electron beams. Modulation of the total energy flux during growth of amorphous TMD material to develop purely amorphous materials or materials with nanoscale nuclei was employed by the authors to examine effects of pre-existing nuclei on crystallization kinetics (i.e., activation energy) and the resulting optical properties. We correlate the wavelength and intensity of photoluminescence from WSe₂ deposited on plasma treated and as-received flexible substrates and present techniques to control film continuity and the areal density of free edges from islands on discontinuous films for tuning the intensity of optical emission. A significant increase in photoluminescence intensity is accompanied by a change in domain boundary density, correlating well to theory. Furthermore, examination of quantum confinement effects by producing nanoscale crystalline areas (between 5-50 nm) with precisely controlled volumes via electron beam radiation provides insight on light emission mechanisms.

12:00pm EM+AN+MI+SS-WeM-13 Polarity Control of GaN Nanowires on Diamond: Experiment and Theory, Karin Larsson, Uppsala University, Sweden; M Hetzl, M Kraut, T Hoffmann, M Stutzmann, Technical University Munich, Germany

III-nitride nanowires on diamond substrates are of current interest for two different potential applications: (i) selectively grown n-type AlGaN nanowires on p/i – diamond are promising for the electrical control and the efficient optical and electrical readout of individual NV-centers in diamond as qubits and (ii) AlGaN/diamond n/p-heterodiodes are an interesting option for future ultraviolet LEDs and laser diodes. For both applications,

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the polarity of AlGaN nanowires grown on diamond has a strong influence on the optoelectronic properties of the heterojunctions, because the polarization-induced interface charge strongly influences the details of the diamond/III-nitride band alignment. Thus, the growth of nanowire arrays with randomly fluctuating polarity will have a negative influence on the electronic properties of the heterojunctions.

In this presentation, we will discuss recent experimental results concerning the control of GaN nanowire polarity on diamond (111) substrates via different surface termination treatments (hydrogenation, oxygen termination, nitrogen radical exposure [1]). Systematic experimental investigations have shown that even very well ordered periodic nanowire arrays deposited by Selective Area Growth exhibit a high degree of polarity disorder. Diamond is a well-suited substrate for these investigations, since it supports several different types of stable surface structures which only differ by about one monolayer and have a strong influence on the preferred nanowire polarity. The effect of different surface terminations on nanowire polarity will be recapitulated. Furthermore, we complement these experimental investigations by theoretically studying the effect of diamond surface termination on the energetically preferred GaN polarity. First principle DFT-calculations are used to calculate the interface energies and the corresponding atomic configurations of the different diamond/GaN interfaces. Strong variations observed in the interface chemistry between diamond and GaN nanowires will be discussed based on the available experimental and simulation data.

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Thin Films Division

Room 102A - Session TF+EM+MI-WeM

Thin Film Processes for Electronics and Optics I

Moderators: Joe Becker, Kurt J. Lesker Company, Virginia Wheeler, U.S. Naval Research Laboratory

8:00am **TF+EM+MI-WeM-1 Crystalline Conductors: Transition Metal Nitride Materials and Device Applications**, *David Meyer, D Katzer, N Nepal, B Downey, M Hardy, D Storm*, U.S. Naval Research Laboratory
INVITED

Development of gallium nitride and related III-N materials thin film growth technology has been instrumental in realizing high performance light-emitting, RF, and power electronic devices for both commercial and military applications. To continue pushing the frontiers of nitride materials research, we have recently incorporated a multi-pocket electron-beam evaporator into our nitride molecular beam epitaxy growth system to enable the evaporation of refractory transition metals. In spite of the complexity of the equilibrium phase diagrams of transition metal nitride (TMN) compounds, we have found that it is possible to grow single-phase TMN thin films epitaxially on SiC and AlN by carefully managing growth kinetics. This talk will discuss our latest results involving TMNs, such as NbN_x and TaN_x, which can be nearly lattice-matched and integrated within III-N heterostructures. Cross-sectional transmission electron microscopy indicates that TMN/III-N interfaces are atomically abrupt with no evidence of interdiffusion of the host elements. We anticipate that the device applications of these metallic films are quite broad ranging from selective etching of sacrificial layers for epitaxial lift-off of processed devices, to buried metallic or superconducting electrodes for quantum computation circuit elements, to optical mirrors and waveguides for improved optoelectronics.

8:40am **TF+EM+MI-WeM-3 Growth Mechanism and Characteristics of Hf-Si-O Film by PE-ALD using TDMAS and TDMAH Precursors and Oxygen Plasma Gas**, *Toshihide Nabatame*, National Institute for Materials Science (NIMS), Japan; *M Inoue*, National Institute for Materials Science (NIMS); *E Maeda, K Yuge, M Hirose*, Shibaura Institute of Technology, Japan; *M Takahashi, K Ito*, Joining and Welding Research Institute, Osaka University, Japan; *N Ikeda*, National Institute for Materials Science (NIMS), Japan; *T Ohishi*, Shibaura Institute of Technology, Japan; *A Ohi*, National Institute for Materials Science (NIMS), Japan

GaN-based power devices with metal-oxide-semiconductor (MOS) structure have been widely investigated for next-generation power devices. To reduce the leakage current, Hf-Si-O has one candidate material among various gate insulators. To fabricate Hf-Si-O film, a HfO₂/SiO₂ laminate film was generally deposited by ALD. The growth mechanism of SiO₂ films was greatly changed by the oxidant gas when Tris(dimethylamino)silane (TDMAS) was as precursor [1]. By using ozone

gas, the stable growth rate and high quality SiO₂ films could be obtained while no growth using H₂O gas. We expect that similar data can be also obtained by using oxygen plasma gas. However, the growth mechanism of the SiO₂ film during HfO₂/SiO₂ laminate film deposition and its characteristics have not been fully understood.

In this study, we systematically investigate growth rate of HfO₂/SiO₂ laminate film by plasma-enhanced ALD (PE-ALD) using TDMAS and Tetrakis(dimethylamino)hafnium (TDMAH) precursors and oxygen plasma gas, and also examine characteristics of the Hf-Si-O films.

The HfO₂/SiO₂ laminate films were deposited on SiO₂/Si substrates by PE-ALD at 300 °C with TDMAH and TDMAS precursors and oxygen plasma gas. The composition Hf/Si ratio of the HfO₂/SiO₂ laminate films were varied by changing each number of ALD cycle. The SiO₂ film was also deposited on SiO₂/Si and HfO₂/Si substrates by the same PE-ALD condition. The Hf-Si-O films were formed by post-deposition annealing (PDA) at 700 – 900 °C in a N₂ atmosphere. The growth per cycle (GPC) of the HfO₂/SiO₂ laminate, HfO₂, and SiO₂ films was estimated by spectroscopic ellipsometry, XPS, and cross-sectional TEM measurements. The structure of Hf-Si-O films was identified by XRD analysis, and electrical characteristics of capacitors with Hf-Si-O films were examined using capacitance – voltage measurement.

The GPC of the HfO₂/SiO₂ laminate, HfO₂, and SiO₂ films on SiO₂/Si substrates were found to be 0.08, 0.08, and 0.04 nm/cycle, respectively, regardless of Hf/Si composition ratio. Considering to the GPC of the HfO₂ (0.08 nm/cycle), the estimated GPC of a SiO₂ layer during HfO₂/SiO₂ laminate film deposition was 0.08 nm/cycle, which was unexpected, but increased by about 2 times compared to that of SiO₂ film on SiO₂/Si substrate. This suggest that an initial adsorption of TDMAS precursor on the SiO₂ and HfO₂ films must be different and strongly affects to the GPC. The Hf-Si-O films (Hf/Si=2/1) maintains amorphous structure even after PDA temperature at 900 °C. The Hf-Si-O films (Hf/Si=2/1) exhibited high dielectric constant of around 14 as expected.

Reference

[1] L. Han, and Z. Chen, *ECS J. of Solid State Sci. and Technol.*, 2 N228 (2013).

9:00am **TF+EM+MI-WeM-4 Atomic Layer Epitaxy of Ultra-wide Bandgap Ga₂O₃ Films**, *Virginia Wheeler, N Nepal*, U.S. Naval Research Laboratory; *L Nyakiti*, Texas A&M University; *D Boris, S Walton, B Downey, D Meyer, C Eddy Jr.*, U.S. Naval Research Laboratory

Ga₂O₃ has emerged as a promising material for next generation power electronics and UV photodetectors applications due to its large bandgap (4.9 eV) and the availability of affordable native substrates from melt-grown bulk crystals. While β-Ga₂O₃ (monoclinic) is the most stable and studied of five polymorphs, the slightly less energetically favorable α- and ε-Ga₂O₃ phases have unique characteristics that can be exploited. The α-Ga₂O₃ (rhombohedral corundum) has the largest bandgap of 5.3 eV and can be alloyed with α-Al₂O₃ and α-In₂O₃ for bandgap engineering. The ε-Ga₂O₃ phase (hexagonal wurtzite) is a polar phase, with a calculated polarization strength that is 10 and 3 times larger than that of GaN and AlN, respectively. Like the III-N system, polarization induced charges can lead to higher charge densities and mobilities in two-dimensional electron gases formed at heterojunctions, which would improve the viability of Ga₂O₃ electronic devices. In this work, we use atomic layer epitaxy (ALEp) to produce high-quality homo- and heteroepitaxial Ga₂O₃ films and investigate phase selectivity as a function of substrate type and orientation, growth temperature (T_g), plasma gas phase chemistry and gas pressure.

All ALE Ga₂O₃ films were deposited in a Veeco Fiji G2 reactor equipped with a load lock and turbo pump using trimethylgallium and O₂ plasma precursors. Initial studies on c-plane sapphire substrates showed that decreasing chamber pressure an order of magnitude during the plasma step resulted in a shift from pure β-Ga₂O₃ to pure α-Ga₂O₃. Additionally, at 350°C and 8 mTorr, the phase could be altered by a varying the O₂ plasma flow from 5-100 sccm. Optical emission spectroscopy indicate that the ratio of O*/O₂ is critical for phase selectivity while the high ion flux to the surface can contribute to the crystallinity at low T_g. By varying T_g from 300 to 500°C at 8 mTorr, films went from mixed β/ε phase at <350°C, to pure α-Ga₂O₃ at 350°C, to pure β-Ga₂O₃ at 500°C. Using the optimum growth conditions for α-Ga₂O₃ on c-sapphire, the influence of substrate was explored using a variety of substrates including AlN, GaN (bulk and epilayers), SiC, diamond, and Si. Deposition on III-N and β-Ga₂O₃ substrates all resulted in crystalline β-Ga₂O₃ films, while amorphous films were deposited on both SiC and Si. This suggests that a clean crystalline substrate interface is critical to obtaining high quality films and promoting metastable phases is more dependent on growth parameters than underlying crystal symmetry. Finally, we will discuss simple electrical

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properties of optimum films of each phase to validate feasibility of the process in device applications.

9:20am **TF+EM+MI-WeM-5 Effects of Process Gases and Gate TiN Masoda during the Post Deposition Anneal to ALD-Al₂O₃ Dielectric Film, Masaya Saito, A Teramoto, T Suwa, K Nagumo, Y Shiba, R Kuroda, S Sugawa, Tohoku University, Japan**

We investigated effects of a post deposition anneal(PDA) to Al₂O₃ film which was formed by the low temperature atomic layer deposition(ALD)⁽¹⁾.

Al₂O₃ films were formed at 75°C by the ALD process using Al(CH₃)₃ as a precursor and H₂O as an oxidant, and these thicknesses were 40 nm. TiN films were formed as gate electrodes of MIS capacitors. We applied three kinds of PDAs. N₂ and O₂ annealing at 400°C were applied just after the ALD(PDA I (a), (b)), and N₂ annealing at 400°C was applied after the gate electrode formation (PDA II). We measured C-V and I-V characteristics.

The negative V_{FB} compared to the ideal one(+0.54 V) was observed in the C-V curve without PDAs, and the fixed charge density calculated from V_{FB} was ~10¹³ cm⁻². In contrast, positive V_{FB} compared to the ideal one was

observed in the C-V curve with PDA I (b), and the fixed charge density was ~10¹¹ cm⁻². These results indicate that PDA I (b) is effective to decrease the fixed charges. Moreover, the hysteresis in the C-V curve decreased by PDA I (b), and the leakage current also decreased within the voltage range of C-V measurement. It is considered that the decrease of hysteresis was caused by decreasing the electrons that were trapped in the Al₂O₃ film⁽²⁾.

However, a few samples broke down at low voltage after PDA I (b). In contrast, we couldn't measure the C-V characteristics of almost capacitors with PDA I (a) because the capacitors broke down at low voltage. In the case of PDA II, which means N₂ annealing after the gate electrode formation, the leakage current decreased same as PDA I (b) and the production yield was still good even after PDA II. This was different tendency from PDA I (a) even as the same annealing. However, V_{FB} shifted to the positive voltage by the PDA II, and the fixed charge density was ~10¹² cm⁻². This was the same phenomenon as the PDA I (b).

We considered these phenomena as follows; the oxidizing species were desorbed by PDA just after the ALD, and then the film quality was bad after the N₂ annealing. The oxygen for improving the film was supplied by the O₂ annealing with the desorption. When PDA was carried out after the gate electrode formation, the desorption did not occur because of capping by the gate electrode, and then the oxidizing species were sufficient for improving the film by the annealing.

Reference:

(1) Y. Koda, et al., *ECS Trans.*, **72**(4), 91-100 (2016)

(2) L. Sambuco Salomone, et al., *J. Appl. Phys.*, **123**, 085304 (2018)

Acknowledgement:

This work was carried out at fluctuation free facility of New Industry Creation Hatchery Center, Tohoku University.

9:40am **TF+EM+MI-WeM-6 Controlling the NbO_x Materials System for Neuromorphic Computing, Alexander C. Kozen, U.S. Naval Research Laboratory; Z Robinson, A Rowley, The College at Brockport - SUNY; T Larrabee, M Twigg, H Cho, S Prokes, U.S. Naval Research Laboratory**

The niobium oxide system has seen recent interest, particularly due to its potential use as both a non-volatile, in the case of Nb₂O₅, or volatile, in the case of NbO₂, memristor material. Nb₂O₅ is a high k dielectric (k~41) with a high refractive index (n~2.2) and a wide bandgap (3.5 eV), while NbO₂ is a thermochromic material with a lower bandgap (1.2 eV) that undergoes a first order crystalline phase transition at a critical temperature (T_c) of 800°C. Both of these phases, along with their intermediate sub-oxides, can serve as material components of memristors to facilitate low-power neural computing hardware.

We will examine the impact of annealing temperature, duration, and atmospheric chemistry on the phase selectivity of the NbO_x thin films fabricated using atomic layer deposition. Anneals of stoichiometric amorphous Nb₂O₅ films are kinetically limited by both Nb⁵⁺ to Nb⁴⁺ reduction and crystallization steps, and we find that the addition of H₂ during annealing is critical for the Nb⁵⁺ to Nb⁴⁺ reduction. To remove this kinetic-limiting step, we instead deposit reduced amorphous NbO₂ films, which crystallize at lower temperatures. We investigate the optical and electrical properties of both amorphous and crystalline NbO_x films and discuss the utility of the NbO_x materials system to the fabrication of memristor materials.

11:00am **TF+EM+MI-WeM-10 Sputtering Power Dependent on Switching Characteristics of ZnO-based Transparent Resistive Memory Devices, Firman Mangasa Simanjuntak, Tohoku University, Japan; T Ohno, Oita University, Japan; S Samukawa, Tohoku University, Japan**

Transparent resistive random access memory (T-RRAM) devices have great potential as data storage for invisible electronics.¹ ZnO material is one of the promising candidates for T-RRAM application due to its high transparency to the visible light.² However, ZnO is an *n*-type semiconducting material which the intrinsic donor defects exist abundantly; consequently, the ZnO-based switching devices require high current compliance to operate as compared to another oxide system.^{1,3} The employment of the high current compliance is to facilitate the formation of conducting filament. Various efforts have been made to improve the ZnO-based switching memories, such as: by controlling the thickness, introducing a dopant(s), adjusting the gas ambient during deposition, stacking with various material(s) and structure(s).¹ However, modulating the switching characteristics by controlling the sputtering power is still less overlooked. In this work, we investigated the influence of sputtering power in resistive switching characteristics of ZnO-based T-RRAM devices.

An approximately 50 nm thickness of ZnO films were deposited onto Indium Tin Oxide (ITO)-coated transparent substrates using conventional RF sputtering. Various sputtering power was used for the deposition while Ar/O₂ ambient is maintained at 2/1 ratio. The deposition rate was measured using a surface profilometer. In order to fabricate sandwich device structure, circular gallium-doped ZnO (GZO) top electrodes were deposited onto the ZnO/ITO structure; patterned using a metal shadow mask with 150 μm in diameter. X-ray diffraction and X-ray photoelectron spectroscopy were used to investigate the crystal structure and the defect concentration of the ZnO films, respectively. A semiconductor device analyzer was used to measure the electrical characteristics of the devices.

XRD pattern indicated that all ZnO films show (002) oriented crystals. The devices made with higher sputtering power showed lower leakage current for OFF state and lowered current compliance to form the conducting filament (for ON state). We also found that the donor defects (oxygen vacancies and zinc interstitials) decrease as the sputtering power increases. These findings indicate that the sputtering power parameter cannot be simply overlooked in the T-RRAM fabrication.

References

¹ F.M. Simanjuntak, D. Panda, K. Wei, and T. Tseng, *Nanoscale Res. Lett.* **11**, 368 (2016).

² F.M. Simanjuntak, O.K. Prasad, D. Panda, C.-A. Lin, T.-L. Tsai, K.-H. Wei, and T.-Y. Tseng, *Appl. Phys. Lett.* **108**, 183506 (2016).

³ T. Ohno and S. Samukawa, *Appl. Phys. Lett.* **106**, (2015).

11:20am **TF+EM+MI-WeM-11 Influence of Intrinsic and Extrinsic Dopants in HfO_x Films for Resistive Switching Memory, SungYeon Ryu, Y Kim, Seoul National University of Science and Technology, Republic of Korea; W Park, S Kim, SK Hynix Inc., Republic of Korea; B Choi, Seoul National University of Science and Technology, Republic of Korea**

Bipolar type resistive switching random access memories (RRAMs) utilized by TaO_x and HfO_x as switching materials, have been demonstrated superior to unipolar type RRAMs owing to the low switching current and better reliability. Bias-polarity-dependent valence change mechanism in HfO_x is attributed to the repeated generation and rupture of conducting filaments (CF), which could be the clusters of oxygen vacancies (V_o). As the device size scales down to 2x nm, the dimension of CF and the whole device area become comparable, and thus the involvement of oxygen loss or unintended V_o incorporation, that is, intrinsic defects may significantly degrade the device reliability. On the other hand, extrinsic defects by doping metallic elements may also change the switching characteristics and device variability depending on the fabrication methods, such as, co-sputtering, implantation, thermal and photo-assisted diffusion, etc.

In this study, influence of both intrinsic and extrinsic defects was investigated systematically. The device having TiN contact-plug with 28 to 2000-nm-diameter formed in SiO₂ inter-layer was fabricated. 1.2-nm-thick HfO_x layer was deposited by atomic layer deposition (ALD). At first, for the control of intrinsic defect, the fabricated RRAM devices were post-annealed in both air and vacuum (~10mTorr) at a wafer temperature of 150 to 250 °C for 20 min, respectively. Electrical property is measured by semiconductor parameter analyzer (HP-4155) and function generator (AFG-3102) for DC and AC measurements. More reliable switching and free-from

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abnormal switching behavior, such as reset-failure, were observed in the vacuum-annealed device.

Secondly, Al- and Ga-doped HfO_x films are grown by using thermal ALD to change the structural and chemical properties of HfO₂ film via incorporating extrinsic defects. Dopant concentration and location were controlled by the ALD cycle ratio and sequence. Through Al doping, pristine resistance and forming voltage of the device were increased with increasing Al cycle ratio. On the other hand, Ga-doped HfO₂ device showed reverse switching polarity. The resistive switching characteristics caused by intrinsic and extrinsic defects in HfO_x films will be presented in detail.

Acknowledgment

This paper was result of the research project supported by SK hynix Inc.

11:40am TF+EM+MI-WeM-12 Scaling up of an Electrochemical Atomic Layer Deposition of Copper, *D Dictus*, Lam Research Corporation, Belgium; **Aniruddha Joi**, Lam Research Corporation; *G Alessio Verni*, Lam Research Corporation, Belgium; *K Vandersmissen*, Imec, Belgium; *B Frees*, Lam Research Corporation, Belgium; *D Yezdi*, Lam Research Corporation

Just like atomic layer deposition in the gas phase, electrochemical atomic layer deposition in the liquid phase holds the promise of delivering very good conformality and uniformity for nm-thick film deposition by using surface limited reactions. Up to today however, there is no industry in which such process has been scaled up from cm-size coupons to industrial-scale substrates. In this paper, the scale up of electrochemical ALD of Cu is reported and it is demonstrated that this process can be used to fill <20 nm Cu interconnect lines as required for future microchip technology nodes.

The e-ALD process is a cyclic process that consists of a step in which a monolayer of Zn is deposited at a potential below the one, at which, Zn would grow multilayers (underpotential deposition), followed by a step in which the zinc is spontaneously displaced by Cu when the substrate is allowed to drift to the open circuit potential (surface limited replacement reaction, SLRR). By cycling between potentiostatic Zn deposition and open-circuit steps, Cu films can be grown in layer-by-layer fashion.

In contrast to classical electroplating processes, e-ALD processes do not require significant overpotential to create uniform nucleation. Also, current densities are small since the deposited amount of material per cycle is low. Therefore, the e-ALD process can be used to deposit Cu with atomic layer thickness control on substrates with high resistivity which gives the advantage of being able to plate on very thin (sub-20 Å) liner materials.

Development of the e-ALD process is done on a Sabre electroplating tool from Lam Research on 300 mm substrates. These substrates contain a thin layer of Ru or Co on which the copper is deposited. The e-ALD process forms the seed layer for further metallization of the interconnect or can by itself fill the narrow interconnect lines.

We will demonstrate that good thickness uniformity can be achieved on 300 mm substrates with initial sheet resistance up to 1000 Ohm/sq and that filling of interconnect lines with dimensions smaller than 14 nm is achieved. Test chips containing our new Cu deposition process show high yield and the Cu interconnect lines have low resistance. This demonstrates the potential use of this new production method in future technology nodes.

12:00pm TF+EM+MI-WeM-13 A Novel High-deposition-rate PECVD Process based on Hollow Cathode Plasma Technique, *S Shayestehaminzadeh*, *N Rivolta*, AGC Glass Europe, Belgium; *M Datz*, Interpane E&B GmbH; *John Chambers*, AGC North America; *H Wiame*, AGC Glass Europe, Belgium

AGC Plasma has recently developed a hollow cathode plasma device as part of its activity as the industrial vacuum equipment manufacturing segment of AGC. This device has been successfully scaled up in order to perform the Plasma Enhanced Chemical Vapor Deposition (PECVD) processes for the coatings on the glass sizes ranging from a few square-centimeters up to a few square-meters (jumbo-sized glass plates 3.2 x 6.0 m²). Plasma generation is undergone between multiple linear hollow cathode cavities, alternately driven by commercially available mid-frequency AC or pulsed power. This enables the generation of a dense and uniform plasma inside the cavities as well as outside of the cavities through the linearly located holes where a less dense plasma (as compared to inside the cavity) but still dense enough, can be utilized in order to activate the reaction between precursor and reactive gases in the depositing chambers.

This geometry and condition allow the system to be scalable to relevant sizes for any typical vacuum processes.

The selected plasma generation method does not require magnets incorporated into the source. This will allow a simplified cooling system within the plasma source, as well as the possibility for adding other magnets to be positioned within the process chamber for modifying the plasma geometry. Based on plasma and vacuum simulations, the electrode-cavity design has been dramatically improved and can be driven by various gases, such as oxygen, nitrogen, argon, helium, and hydrogen. Plasma operation is also possible in an extremely wide range of pressures from 1 mTorr to 1 Torr, while the most useful process pressures for PECVD are generally in the 1 mTorr to 30 mTorr range. The wide hollow cathode pressure operation range allows for the deposition of multilayer coating stacks by magnetron sputtering and PECVD in the same vacuum coating lines.

Electrode faces have also been enhanced using surface coatings to avoid erosion during high power operation, also reducing subsequent debris and extending source lifetime. Depending on the choice of precursor materials, the desired film properties, and in-chamber magnetic field geometries, dynamic deposition rates for inline PECVD coatings of 200-500 nm³/m/min

have been demonstrated for SiO₂ on flat glass products however by selecting different gases and precursors various materials can be deposited using the same source line. This unique process opens a new range of possibilities to be investigated for a variety of substrates. These plasma sources are now commercially available in either lab or industrial sizes to explore new applications.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 202A - Session SA+AS+MI-WeA

Hard X-Ray Photoemission for Probing Buried Interfaces

Moderators: Zahid Hussain, ALS-LBNL, Olivier Renault, CEA-University Grenoble Alps, France

2:20pm SA+AS+MI-WeA-1 Element-resolved Electronic Band Structure of Ga(Mn)As Measured by Standing-wave Hard X-ray Angle-resolved Photoemission, Slavomir Nemsak, Advanced Light Source, Lawrence Berkeley National Laboratory; *M Gehlmann, C Kuo,* University of California, Davis; *T Lee,* Diamond Light Source Diamond House, Harwell Science and Innovation Campus; *L Plucinski,* Forschungszentrum Juelich GmbH, Germany; *J Minar,* University of West Bohemia; *C Schneider,* Forschungszentrum Juelich GmbH, Germany; *C Fadley,* University of California, Davis

Electronic band structure of the dilute magnetic semiconductor $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ was obtained using hard X-ray angle-resolved photoemission. The element- and site-sensitivity of the measurements was achieved by forming a strong X-ray standing-wave generated by Bragg reflection from the (111) atomic planes of both undoped GaAs and Mn-doped thin films. Due to the uneven occupancy of (111) planes by either Ga(Mn) or As atoms, the element-specific band structure can be obtained with a help of the SW modulation in core levels. Measured momentum- and element-resolved bulk electronic structure was compared to element-projected Bloch spectral functions with excellent agreement between experiment and theory. Apart from the site specific decomposition of the electronic structure, the SW measurements also confirmed a substitutional presence of Mn atoms at the Ga sites. This novel technique should be applicable to a broad range of complex materials.

2:40pm SA+AS+MI-WeA-2 Probing Surface Band Bending of Polar GaN by Hard X-ray Photoemission Combined with X-ray Total Reflection, Shigenori Ueda, NIMS, Japan

GaN is known as a polar semiconductor due to an alternative stacking of Ga and N layers along the c-axis. Ohsawa *et al.* [1] showed the difference in valence band spectral shapes of the bulk Ga- and N-polar GaN single crystals by using polarization dependent hard X-ray photoemission spectroscopy (HAXPES). In general, HAXPES is a bulk-sensitive probe [2], and take-off angle (TOA) dependent of photoelectron gives depth information [3]. However, the decrease of the photoemission intensity occurs in lower TOA, and the valence band spectra depend on TOA [3] due to the matrix element effect [4].

In this work, HAXPES combined with X-ray total reflection was used to obtain a depth-resolved electronic structure instead of TOA dependent measurements. The change of incidence angle within 1 degree around the critical angle of X-ray total reflection drastically changes the attenuation length of X-ray in solids.

We have measured the core-level and valence band HAXPES spectra of commercially available bulk single crystalline GaN for Ga and N polar faces in the case of inelastic mean free path of 2.17, 3.73, and 7.69 nm. Undoped n-type GaN crystal with fine polished surfaces was used. For the Ga-polar face, large band bending behavior was observed, while the band bending was small for the N-polar face. The Ga 3s and N 1s core-level spectra also showed the polarity dependent band bending behavior. We found that

GaN near the surface is degraded in both the polar faces. This result suggests that high quality single crystalline GaN with fine surface treatment is required for detecting the intrinsic electronic structure of GaN. Finally we note that HAXPES combined with X-ray total reflection is useful method for depth-resolved electronic structure measurements, since the data acquisition time in this method is 10 or more faster than that in TOA dependent measurement, and the matrix element effect is almost negligible in this method.

References

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- [3] M. Lozac'h *et al.*, Sci. Technol. Adv. Mater. **14**(2013) 015007.
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3:00pm SA+AS+MI-WeA-3 Interfaces in Cycled Battery Electrodes: Insights from HAXPES Studies, Julia Maibach, Karlsruhe Institut of Technology (KIT), Germany

INVITED

Rechargeable ion batteries such as lithium and sodium ion batteries generally consist of a negative electrode, a positive electrode and an ion conducting electrolyte. The contacts between the different materials are key to the electrochemical energy storage process and at the surfaces of the electrodes and at the interfaces to the electrolyte, reactions crucial to long-term, safe battery operation take place. Due to its surface and chemical sensitivity, photoelectron spectroscopy has therefore become a widely used tool to characterize and understand the processes and phenomena in these electrochemical energy storage systems.

Looking in more detail, a battery electrode itself is a complex system as it consists of many different components such as the active storage material, conductive additives as well as binders to keep the particles attached to a metal foil, which acts as a current collector. This complexity of mixed materials and morphologies further increases when the electrodes are cycled electrochemically due to the desired storage processes and due to reactions with the battery electrolyte leading to interface layer formation.

These highly complex systems of cycled battery electrodes bring new challenges when studied with photoelectron spectroscopy. In this presentation, observed peak shifts for cycled battery electrodes will be discussed in depth. Particular emphasis will be given to the buried interfaces. Here, hard x-ray photoelectron spectroscopy (HAXPES) is one of the few available techniques that can access the buried interface while maintaining the chemical information from the delicate battery interface layers. Based on HAXPES experiments, the role of the buried interfaces and their importance in both battery operation as well as in photoelectron spectroscopy characterization of cycled electrodes will be discussed.

Additionally, spectral changes due to electrode potentials as well as lithiation effects will be discussed. These strongly depend on the nature of the active material and therefore need to be considered carefully to achieve consistent data interpretation. Combining all presented effects, a strategy for photoelectron spectroscopy experiments on cycled battery electrodes will be proposed that takes buried interfaces into account.

4:20pm SA+AS+MI-WeA-7 Development of Ambient Pressure HAXPES and other HAXPES Measurements at SPring-8 for Buried Interface, Yasumasa Takagi, Japan Synchrotron Radiation Research Institute (JASRI), Japan

INVITED

A near ambient pressure photoelectron spectroscopy measurement that use with hard X-rays (AP-HAXPES) were conducted at the BL36XU of SPring-8. The AP-HAXPES system with a commercial differential pumping-type spectrometer (R4000 HiPP-2, Scienta Omicron Inc.) was installed in the beamline. The excitation light of 7.94 keV focused to a beam size of 20 μm x 20 μm on the sample surface was used. The standard aperture size at the top of the front cone in the spectrometer is a diameter of 300 μm . In this report, we replaced the front cone with our home-made one with an aperture diameter of 30 μm to increase the pressure limit in the AP-HAXPES measurement. Meanwhile, we have adapted the working distance of 60 μm in order not to perturb the gas environment at the sample surface.

We measured the XPS spectra of the Au(111) surface grown on a mica substrate under various gas pressures using the AP-HAXPES equipment. The intensity decay of the Au 4f spectra with an increasing gas pressure from 1 Pa to 100 kPa. Here we use "100 kPa" as the atmospheric pressure. The XPS measurement was not affected by the ambient gas at a pressure of 1 Pa. As the gas pressure increased, the signal intensity decreased because the photoelectrons were scattered by the ambient gas while passing through the sample to the detector. Although the signal intensity was very weak at the atmospheric pressure, the peaks of $4f_{5/2}$ and $4f_{7/2}$ can be detected. The signal-to-noise ratio can be improved by a prolonged acquisition time. The $4f_{7/2}$ and $4f_{5/2}$ peaks are clearly found in the spectrum at the atmospheric pressure in an acquisition time of 30 min. The Shirley background was subtracted from the spectrum, and the plots were fitted with a Voigt function. The curve fitting result shows that the energy difference between the $4f_{7/2}$ and $4f_{5/2}$ peaks is 3.7 eV and the intensity ratio $4f_{7/2}:4f_{5/2}$ is almost 4:3. These values are in good agreement with the standard value of the Au 4f peaks. Thus, a photoelectron spectroscopy under atmospheric pressure was successfully obtained using an aperture of 30 μm .

Wednesday Afternoon, October 24, 2018

5:00pm **SA+AS+MI-WeA-9 Operando HAXPES Investigations of La Manganite-based Resistive Memories**, *Eugénie Martinez*, CEA/LETI-University Grenoble Alpes, France; *B Meunier*, Univ. Grenoble Alpes, CEA, LETI & LMGP, CNRS, France; *D Pla*, Univ. Grenoble Alpes, LMGP, CNRS, France; *R Rodriguez-Lamas*, Univ. Grenoble Alpes, LMGP, CNRS France; *M Burriel*, *C Jimenez*, Univ. Grenoble Alpes, LMGP, CNRS, France; *J Rueff*, Synchrotron SOLEIL, France; *Y Yamashita*, *S Ueda*, NIMS, Japan; *O Renault*, CEA/LETI-University Grenoble Alpes, France

The use of perovskite oxides in resistive random access memories (RRAMs) is considered for the next generation of non-volatile memories (NVMs) [1]. Indeed, their highly tunable ionic and electronic transport properties open new possibilities for multilevel storage capacity. In particular, manganese oxides, such as LaMnO_{3+d} (LMO), are among the most promising candidates [2]. The switching mechanism is related to oxygen transport, yielding to the creation and annihilation of oxygen vacancies through the functional layer. However, two main mechanisms based on filaments or 2D interfacial effects must be discriminated to better understand and control the devices properties.

We investigate here the key role of oxygen in the switching mechanism of LMO-based RRAMs using hard X-ray photoelectron spectroscopy (HAXPES). This technique allows learning about electrochemical reactions involved in the structure with sufficient depth sensitivity. Operando HAXPES was performed at Soleil and Spring-8 to investigate in-situ resistive switching. Measurements were done while biasing the memory with opposite polarities, to reach successively low and high resistance states. In particular, a chemical analysis of the interface between the active electrode and the LMO was done after *Set* and *Reset* operations.

Results show modifications of the oxygen core level spectra. The peak assigned to interfacial LMO shifts as a function of bias voltage, contrary to the bulk LMO component. These results highlight variations in charges concentration at the electrode/LMO interface, as a result of creation/annihilation of interfacial defects, such as oxygen vacancies. Complementary trends regarding $\text{La}3d$ and $\text{Mn}3s/2p$ spectra will be discussed in terms of oxidation and reduction phenomena, related to variations of the oxygen content at the electrode/LMO interface.

[1] Jin YL, Jin KJ, Ge C, Lu HB, Yang GZ, Resistive switching phenomena in complex oxide heterostructures, *Modern Physics Letters B*, 2013;27(29)1330021.

[2] Pan F, Gao S, Chen C, Song C, Zeng F, Recent progress in resistive random access memories: Materials, switching mechanisms and performance, *Mater. Sci. Eng. R* 2014,83:1-59.

5:20pm **SA+AS+MI-WeA-10 Combining Hard and Soft X-ray Angle-resolved Photoemission to Probe the Bulk Electronic Structure of Engineered Quantum Solids**, *Alexander Gray*, Temple University **INVITED**

Angle-resolved photoelectron spectroscopy, or ARPES, is a powerful and well-established experimental technique for probing the momentum-resolved electronic structure of matter. In this talk, I will discuss several promising new directions in this field, which stem from experimental and theoretical studies wherein angle-resolved photoemission is carried out at higher excitation energies, namely in the soft and hard x-ray regimes. I will focus specifically on the recent studies of novel engineered quantum materials and heterostructures, which aim at gaining a clear understanding of the depth-dependent nanoscale evolution of materials' electronic properties at the surface, in the bulk, and across the buried interfaces by using multiple modalities of hard and soft x-ray angle-resolved photoemission both separately and in tandem with each other.

6:00pm **SA+AS+MI-WeA-12 Surface/Interface Coupling in Buried Oxide Interfaces**, *Conan Weiland*, National Institute of Standards and Technology (NIST); *A Rumaiz*, Brookhaven National Laboratory; *G Sterbinsky*, Argonne National Laboratory; *J Woicik*, National Institute of Standards and Technology (NIST)

Oxide interfaces can host a variety of properties not found in the bulk materials. The interface between LaAlO_3 (LAO) and SrTiO_3 (STO) is a prototypical example; the interface of these two insulators can show conductivity, ferromagnetism, and even superconductivity. The source of these interface properties is still a matter of debate, with potential explanations including electronic reconstruction due to the polar discontinuity at the interface, chemical intermixing, and oxygen vacancies at either the interface or LAO surface. Hard x-ray photoelectron spectroscopy (HAXPES) is an excellent tool to probe these interfaces due to the enhanced and tunable probe depth afforded by a synchrotron source. We have used a combination of variable kinetic energy HAXPES and

ambient pressure soft x-ray photoelectron spectroscopy (AP-XPS) to investigate the interplay between LAO film and surface structure and the LAO/STO interface. We find Al surface enrichment for most LAO films, while AP-XPS shows significant band shifts in the presence of water vapor. The role of these LAO surface features on the LAO/STO interface conductivity will be discussed.

Thin Films Division

Room 102A - Session TF+EM+MI-WeA

Thin Film Processes for Electronics and Optics II

Moderators: Hilal Cansizoglu, University of California, Davis, John F. Conley, Jr., Oregon State University

2:20pm **TF+EM+MI-WeA-1 What can we Benefit from Nanochemistry of Crystalline Silicon?**, *Naoto Shirahata*, National Institute for Materials Science, Tsukuba, Japan **INVITED**

The richly tunable optical properties of colloidal silicon nanoparticles, in conjunction with flexible functionalization of their surfaces, makes them important class of materials with various potential applications in the ranging from medicine to optoelectronics. Bulk crystal of silicon is an indirect bandgap semiconductor, resulting in poor light emission and a weak absorption onset – major technological barrier for their use in photonics. The successful approaches in transforming silicon into efficient light emitters are appearance of the quantum confinement effect and reformation in atomic structure and periodicity from diamond cubic lattice to nanoclusters having a direct gap structure. The improved optical properties including photoluminescence quantum yields, require the efficient radiation recombination between photogenerated electron-hole pairs across the gaps. To achieve this, the surface chemistry plays an important role. In particular, the formation of carbon-silicon linkage at the surface of the nanoclusters results in the enhanced radiative recombination probability.

Today's talk starts by describing a brief overview of light emitting silicon nanoparticles to understand their place in the world of colloidal semiconductor nanocrystals. Next, the talk focuses on the reliable approaches to give a fine tuning of photoluminescence spectra with high spectral symmetries and impressively narrow spectral linewidths. Recent progress of chemical synthesis and surface functionalization of silicon nanoparticles is then demonstrated, in conjunction with their applications including efficient light emitting diodes and non-toxic biomarkers adapted for two-photon excitation fluorescence cell imaging. The performance of silicon-based light emitters are influenced significantly by surface moiety.

Since the finding of porous silicon in 1990, the free-standing, strongly luminescent silicon nanoparticles have become a masterpiece of nanoscience and nanochemistry. Such thermodynamically-stable colloidal nanoparticles will continue to lead to novel concepts of medical and device applications in near future.

3:00pm **TF+EM+MI-WeA-3 Low-temperature Homoepitaxial Growth of Two-dimensional Antimony Superlattices in Silicon**, *April Jewell*, *M Hoenk*, *A Carver*, *S Nikzad*, Jet Propulsion Laboratory

Our group has previously reported on the growth of antimony delta-doped silicon by low-temperature molecular beam epitaxy. In this presentation we will discuss the extension of our antimony delta doping capabilities to the growth of n-type superlattices (i.e. films that incorporate multiple delta layers). We will discuss details related to growth optimization, and show results from in situ monitoring by Auger electron spectroscopy and electron diffraction. We will also report on electrical characterization of our films and preliminary device measurements.

JPL's delta doping and superlattice doping (i.e., two-dimensional "2D" doping) processes have been developed primarily for use with silicon-based scientific imagers. A key performance metric for these detectors is photometric stability, a parameter that depends largely on passivation at the detector interface. Our approach uses an atomically thin (2D), highly concentrated layer of dopant atoms embedded within nanometers of the surface. This allows for dopant concentrations in the range of 10^{13} - 10^{14} cm^{-2} (10^{20} - 10^{21} cm^{-3}); higher than can be achieved with 3D doping techniques.

Resulting quantum effects within the highly-doped 2D layers result in exceptional stability in 2D-doped devices.

N-type 2D-doping with antimony is challenging primarily because it tends to segregate to the surface. Segregation is suppressed at low temperatures; however, this may compromise epitaxial growth and lead to

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poor dopant incorporation and activation. Even so, it has been shown that at sufficiently slow silicon deposition rates it is possible to maintain epitaxial growth even at low temperatures for finite thicknesses. In our previous work with single n-type delta layers, we demonstrated activated dose concentrations as high as $2 \times 10^{14} \text{ cm}^{-2}$ and sharp dopant profiles ($\sim 35 \text{ \AA}$ FWHM). Under the current effort we have further optimized our growth processes to achieve even sharper dopant profiles and multiple delta layers. This is enabled by switching from a standard effusion cell to a valved cracker cell for antimony evaporation, which allows for high atom and carrier densities on the order of $\sim 10^{21} \text{ cm}^{-3}$ with peak distribution at $\sim 10 \text{ \AA}$ FWHM.

The performance of our low-temperature 2D-doping processes has been validated by applying both p-type and n-type superlattice-doping to fully depleted photodiodes. The superlattice-doped devices show significantly higher responsivity than the equivalent ion-implanted devices. Additionally, when exposed to pulsed X-rays the superlattice-doped devices exhibit fast response and recovery times required for use in pulsed power experiments.

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4:20pm TF+EM+MI-WeA-7 Electron-Doped BaZrO₃ Thin Films Prepared by Topochemical Reduction, *Thomas Orvis*, University of Southern California

The nature of surfaces and interfaces plays a key role in governing interfacial charge transfer, which drives electronic and energy applications such as electron emission and catalysis. Low electron affinity materials, either as heavily doped semiconductors or metals, are of interest for these applications. The electron affinity engineering of tailorable material families, such as complex oxide perovskites, can provide a rational route to the development of such low electron affinity materials. BaZrO₃, a cubic perovskite and widely used proton-conducting material, has a very low electron affinity but wide band gap, making traditional donor-doping thermodynamically unfavorable. Here, we report the successful reduction of BaZrO₃ thin films via topochemical reaction using CaH₂. We report the structural characterization and electrical properties of these films before and after reduction. Our studies show that hydride-based reduction is a viable method to induce electron-doping in BaZrO₃, and we discuss the properties and meta-stability of the reduced films using time-dependent property measurements.

4:40pm TF+EM+MI-WeA-8 Epitaxial Growth and Electrical Properties of VO₂ Thin Films, *Yang Liu, S Niu, T Orvis, H Zhang, H Wang, J Ravichandran*, University of Southern California

We report the epitaxial growth and the electrical properties, especially the metal-to-insulator transition (MIT) of vanadium dioxide (VO₂) thin films synthesized on lanthanum strontium aluminate tantalate (LSAT) (111) substrates by a pulsed laser deposition method. X-ray diffraction study shows that the epitaxial relation between the VO₂ thin films and LSAT substrate is given as VO₂(020) || LSAT(111) and VO₂[001] || LSAT[11-2]. We observed a sharp change of four orders of magnitude in resistance at the MIT temperature of 345K. We measured distinctive Raman spectra below and above the transition point indicating a structural transition between the insulator and metallic phases, as observed in past investigations.

5:00pm TF+EM+MI-WeA-9 A Novel Technique for the Growth of Gallium Oxide Nanowires for UV Detection, *Badriyah Alhalaili*, UC, Davis; *R Bunk, H Mao*, UC Davis; *R Vidu*, UC, Davis; *H Cansizoglu*, UC Davis; *M Islam*, UC, Davis

Recently, high interest in wide bandgap semiconductors for a variety of applications has grown. Due to the unique thermal, optical, and electrical properties of Ga₂O₃, the scientists attract to the assessment of Ga₂O₃ nanowires (NWs) as a valuable material in semiconductor research fields, especially for applications in harsh environments and power electronics. Compared to thin films, nanowires exhibit a higher surface-to-volume ratio, increasing their sensitivity for detection. Additionally, nanowire devices exhibit quantum effects not seen in bulk materials and allow for crystalline materials to be grown on arbitrary substrates in spite of lattice mismatch due to lattice strain relaxation at the interface. In this work, we explore a simple and inexpensive method of growing high-density gallium oxide NWs at high temperatures. The gallium oxide NWs growth mechanism can be obtained by heating and oxidizing the gallium metal into high temperatures above 900 °C. This process can be optimized for large-scale production with high-quality, dense and long-length of gallium oxide NWs. We show the results of the characterization of the materials including the optical band gap, Schottky barrier height with metal contacts, and photoconductance of β -Ga₂O₃ nanowires. The influence of density on these Ga₂O₃ nanowires will

be examined in order to determine the optimum configuration for the detection of UV light.

5:20pm TF+EM+MI-WeA-10 Enhanced Efficiency in Photon-trapping Ge-on-Si Photodiodes for Optical Data Communication, *Hilal Cansizoglu, C Bartolo Perez, Y Gao, E Ponizovskaya Devine, S Ghandiparsi, K Polat, H Mamta, M Cansizoglu*, University of California, Davis; *T Yamada*, University of California, Santa Cruz; *A ElRefaie, S Wang*, W&WSens Devices, Inc.; *S Islam*, University of California, Davis

High speed, surface illuminated Ge-on-Si *pin* photodiodes with improved efficiency are fabricated and characterized. External quantum efficiency (EQE) of the Ge-on-Si *pin* diode is enhanced to >80% at 1300 nm and 73% at 1550 nm with only 2 μm thick intrinsic Ge layer, which is required to maintain high speed operation. Improved EQE is achieved by guiding incident light into the device structure with the help of microholes arranged in a lattice with a periodicity at the scale of wavelength. Vertically propagating light is coupled to the lateral modes in the material with periodic holes and absorbed efficiently despite a thin layer. More than 350% of EQE is enhanced by hole arrays compared to the case without holes up to 1700 nm wavelength. Such promising results enable Ge-on-Si photodiodes potentially cover both existing C band (1530 nm-1560 nm) and L band (1560 nm-1620 nm) and a new data transmission window (1620 nm-1700 nm), which can be a solution to capacity crunch of conventional standard single mode fiber (SSMF) cables. CMOS/BiCMOS compatible fabrication of photon-trapping Ge-on-Si photodiodes can lead to integrated transceiver circuits with electronics for cost-effective solutions in various near-infrared sensing applications such as metro and long haul dense wavelength division multiplexing (DWDM) systems, laser radar (LIDAR) systems, quantum communications and near-infrared imaging.

5:40pm TF+EM+MI-WeA-11 Correlating Composition and Structure with Optical Properties of Combinatorial Sputtered Thin Film Au_xAl_{1-x} Alloys, *Robyn Collette*, University of Tennessee Knoxville; *Y Wu, J Camden*, University of Notre Dame; *P Rack*, University of Tennessee Knoxville

Surface plasmon resonances can be sustained by metallic nanostructures and have been explored for potential optoelectronic device applications.

Superior plasmonic properties may be realized by alloying and consequently tuning the LSPR, however, there has been limited work done on alloys for use in plasmonic devices. The alloy behavior greatly depends on the ordering of the structure; thus, it is crucial to explore how the optical properties are related to the structure of the alloy.

In this work, the structure and optical properties of Au-Al thin film alloys were investigated as both individual metals have strong plasmon resonances. Initially, 350 nm thick Au_xAl_{1-x} (0.15 < x < 0.72) was co-sputtered on 100mm x 15mm silicon substrates. Subsequently samples of 0.9 < x < 1 and 0 < x < 0.2 were investigated. Energy dispersive spectroscopy (EDS) was used to measure the composition as a function of position on the substrate for the combinatorial samples. The crystal structure at various compositions were subsequently determined using grazing incidence x-ray diffraction (GIXRD) and the dielectric constants, ϵ_1 and ϵ_2 , were determined via spectroscopic ellipsometry. The evolution of phases was studied by annealing various compositions under vacuum and the optical properties were correlated to observed phases on the equilibrium phase diagram. Lastly, we explore the plasmonic properties of lithographically patterned Au_xAl_{1-x} (0 < x < 0.2). The optical transmission and reflection is measured and compared with electron energy loss spectroscopy results. The phase evolution is studied using a (scanning) transmission electron microscope with an *in situ* laser heating system and the low loss electron energy loss spectra are correlated to the structural changes. Interestingly, we found in the mixed phase region containing Al and AuAl₂ that as the concentration of AuAl₂ increased, an increase of ϵ_1 and a decrease of ϵ_2 around 1.5 eV.

6:00pm TF+EM+MI-WeA-12 The Multifunctional TiO₂ Thin Films Sensor, *Awais Ali, M Alam, S Nasser, N Akbar, A Saeed, A Bhatti*, COMSATS Institute of Information Technology, Islamabad Pakistan, Pakistan

In the present work, multifunctional/hybrid UV and IR sensing was performed by Nd doped TiO₂ thin films. Thin films were sputter deposited and concentrations of dopants was varied in targets. The results suggested that the incorporation of Nd produced compressional stresses in lattice, which resulted in textured growth and asymmetry of bonds as confirmed by XRD and Raman spectroscopy. The dopant driven non-stoichiometry and presence of O vacancies was evident from XPS measurements. The defects and dopant mediated luminescence was obtained in visible and IR regions, respectively. The sensing of UV light was attributed to the host (titania), whereas successful incorporation of dopant helped in sensing IR source.

2D Materials Focus Topic

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

Novel 2D Materials

Moderator: Han Wang, University of Southern California

8:20am **2D+EM+MI+MN+NS+SS-ThM-2 Controlled Growth of 2D Ni-Silicate and Silica Films on Ni_xPd_{1-x}(111) Substrates**, *Chao Zhou, X Liang, G Hutchings, Z Fishman, J Jhang, S Hu, S Ismail-Beigi, U Schwarz, E Altman*, Yale University

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

8:40am **2D+EM+MI+MN+NS+SS-ThM-3 Topological Materials**, *Hsin Lin*, Institute of Physics, Academia Sinica **INVITED**

Topological materials host various novel quantum phases of electrons which are characterized by band topology and topologically protected surface/edge states. Despite recent progress, intense world-wide research activity in search of new classes of topological materials is continuing unabated. This interest is driven by the need for materials with greater structural flexibility and tunability to enable viable applications in spintronics and quantum computing. We have used first-principles band theory computations to successfully predict many new classes of topologically interesting materials, including Bi₂Se₃ series, the ternary half-Heusler compounds, TlBiSe₂ family, Li₂AgSb-class, and GeBi₂Te₄ family as well as topological crystalline insulator (TCI) SnTe family and Weyl semimetals TaAs, SrSi₂, (Mo,W)Te₂, Ta₂S₂, and LaAlGe family. I will also highlight our recent work on unconventional chiral fermions in RhSi and several material candidates for new TCI.

9:20am **2D+EM+MI+MN+NS+SS-ThM-5 Few-Layer Rhenium Disulfide Synthesized Via Chemical Vapor Deposition**, *Michael Valentin*, Army Research Laboratory; *A Guan, A Nguyen, I Lu, C Merida, M Gomez*, University of California, Riverside; *R Burke, M Dubey*, Army Research Laboratory; *L Bartels*, University of California, Riverside

Transition metal dichalcogenides (TMDs) are exciting new materials that have received much attention due to their semiconducting properties in the direct bandgap. Well-studied TMDs, such as molybdenum disulfide (MoS₂) and tungsten diselenide (WSe₂), exhibit a direct bandgap in the monolayer form, but an indirect bandgap in the bulk form. Rhenium disulfide (ReS₂), on the other hand, is a new TMD that is unique in its ability to retain a direct bandgap independent of thickness. By using chemical vapor deposition (CVD), few-layer ReS₂ is synthesized and characterized by optical methods such as Raman spectroscopy and photoluminescence. We also show characterization results for atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), transmission electron microscope (TEM), and electrical transport to determine thickness, crystallinity, homogeneity, and electrical characteristics for use in future flexible electronics.

9:40am **2D+EM+MI+MN+NS+SS-ThM-6 Dipolar Disorder of a van-der-Waals Surface Revealed by Direct Atomic Imaging**, *M Susner*, Air Force Research Laboratory; *M McGuire, Petro Maksymovych*, Oak Ridge National Laboratory

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

Here we present the first atomically resolved imaging of CuScP₂S₆ s carried out using cryogenic non-contact atomic force microscopy. The surface exhibits good crystalline ordering at the atomic scale, revealing contrast on sub-unit cell level. The most remarkable property is long-range commensurate modulation of the surface morphology, with a topographic amplitude of only 2-3 pm. Combined with XRD analysis of the bulk and Monte-Carlo simulation of the Ising model on triangular lattice, we propose that the modulation arises from antiferroelectric polarization domains, albeit with frustrated long-range order. The key structural ingredient for this state is centrosymmetric position of Sc³⁺ within the layer, which forces the surrounding displacing Cu+1 ions to adopt a frustrated antiferroelectric state - in direct analogy frustrated magnetic systems. We will further discuss the peculiarities of nc-AFM imaging of this materials from the statistical analysis of the variation of images between scan, as well as the force-distance curve arrays. The possibility to directly visualize polar order opens broad opportunities to understand the atomistic aspect of ferroelectric, glassy and incommensurate phases in this material class, beginning with CuInP₂S₆ – which exhibits Curie temperature ~315K and giant negative electrostriction [2]. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. Microscopy experiments were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

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

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

11:00am **2D+EM+MI+MN+NS+SS-ThM-10 Advanced ARPES Analyzer and Momentum Microscope KREIOS 150 – Concepts and first results on layered materials and topological insulators**, *Paul Dietrich, M Wietstruck, T Kampen, A Thissen*, SPECS Surface Nano Analysis GmbH, Germany

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

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

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

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real live samples like Graphene on Germanium were measured. Even on macroscopically rough surfaces like Graphene on NbSe₂ excellent ARPES and X-PEEM results could be obtained. By taking advantage of the small spot capability of the KREIOS 150 meaningful band structure data has been recorded on such patchy samples.

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

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

Clean water is a global challenge, and membrane filtration is a key technology to achieve it. Here, we report on carbon nanomembranes (CNMs) with sub-nanometer channels that prove to be excellent water filters, combining a high selectivity with an exceptionally high water permeance. The CNMs are fabricated via the cross-linking of terphenyl self-assembled monolayers [1], resulting in a ~1.2 nm thick membrane perforated by channels with diameters below ~0.7 nm and areal densities of ~10¹⁸m⁻². When tested as filter membranes, it was found that the CNMs efficiently block the passage of most gases and liquids [2]. However, water passes through, and it does this with a record-breaking permeance of ~1.1×10⁻⁴ mol·m⁻²·s⁻¹·Pa⁻¹. This suggests that water molecules translocate fast and cooperatively through the sub-nanometer channels. Assuming all channels in a TPT-CNMs are active in mass transport, we find a single-channel permeation of ~66 water molecules·s⁻¹·Pa⁻¹. We compare this with molecular transport through other carbon nanoconduits, such as carbon nanotubes or membrane proteins (aquaporins). As the fabrication of CNMs is scalable, their utilization opens a path towards the application of 2D-materials in energy-efficient water purification.

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

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

11:40am **2D+EM+MI+MN+NS+SS-ThM-12 Discovery of Dirac Monolayers and Elucidation of Functonalites by Advanced Soft X-ray Spectroscopy**, **Iwao Matsuda**, University of Tokyo, Japan **INVITED**

Vapor deposition of three-dimensional (3-D) crystal on a substrate often results in formation of the novel 2-D materials with intriguing electronic states. The approach has been well-known in the field of "Surface Science", which has attracted our attentions over the past decades. Triggered by fabrication of the graphene layers, researches on such monatomic sheets have extended to various kinds such as silicene, germanene and so on. Soft X-ray spectroscopies, such as photoemission spectroscopy, have been used to directly probe electronic states of monatomic layers and also to examine carrier dynamics under the *operando* condition. We recently observed Dirac Fermions in a 2-D boron sheet, borophene, that forms spontaneously on the Ag(111) surface. Furthermore, we found pairing of the Dirac cones due to Moire-periodic perturbations of the overlayer-substrate interactions. In the Cu₂Si monolayer, we also discovered the 2-D Dirac nodal line fermions that are protected by the mirror reflection symmetry. In the presentation, I will describe details of our research on the novel 2-D Dirac materials and introduce the advanced soft X-ray techniques that reveal their functionalities for developing devices.

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

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

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

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

Nanostructures for Electronic and Photonic Devices

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

8:00am **EM+MI+MN+NS-ThM-1 Extreme Nanophotonics from Ultrathin Metallic Junctions**, **Maiken Mikkelsen**, Duke University **INVITED**
New optical nanomaterials hold the potential for breakthroughs in a wide range of areas from ultrafast optoelectronics such as modulators, light sources and hyperspectral detectors, to efficient upconversion for energy

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

8:40am **EM+MI+MN+NS-ThM-3 The Geode Process: A Route to the Large-Scale Manufacturing of Functionally-Encoded Semiconductor Nanostructures**, M Mujica, G Tutuncuoglu, V Breedveld, S Behrens, **Michael Filler**, Georgia Institute of Technology

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

9:00am **EM+MI+MN+NS-ThM-4 Disordered Microsphere-Based Coatings for Effective Radiative Cooling under Direct Sunlight**, S Atiganyanun, J Plumley, K Hsu, University of New Mexico; T Peng, Air Force Research Laboratory; **Sang M. Han**, S Han, University of New Mexico

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

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

9:20am **EM+MI+MN+NS-ThM-5 Assessing Strain Relaxation in Nanostructured InGaN Multiple Quantum Wells Using X-Ray Diffraction Reciprocal Space Mapping and Photoluminescence Spectroscopy**, *Ryan Ley, C Pynn, M Wang, S DenBaars, M Gordon*, University of California at Santa Barbara

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

This talk will highlight our recent work using colloidal and templated lithography and Cl₂/N₂ plasma etching to fabricate nanoscale InGaN/GaN LED structures (diameter = 150-600nm), and how sub micron scale patterning affects the strain state and optical behavior of MQW emitters. InGaN/GaN LED structures were grown by MOCVD on c-plane sapphire substrates and characterized before and after nanopatterning using on-axis (0002) and off-axis (10-15 and 11-24) XRD reciprocal space maps (RSM), rocking curves and photoluminescence (PL) spectroscopy at 14K. RSM analysis found degrees of relaxation of 30% and 20% for the smallest and largest structures, respectively, and rocking curves revealed a 0.7nm decrease in the InGaN quantum well thickness. These relaxation effects also correlate well with spectral blue shifts (~10-15nm) in the PL, which are supported by 1D quantum mechanical and electrostatic simulations. Overall, this work shows that nanopatterning of InGaN/GaN active emitters at sub-micron length scales can reduce strain related issues in the III-Nitrides and potentially allow higher incorporation of indium for green and red emission.

9:40am **EM+MI+MN+NS-ThM-6 Scalable, Tunable, and Polarization-Independent High Contrast Grating Reflectors for Integration into Resonant-Cavity micro-LEDs**, *Pavel Shapturenka, S DenBaars, M Gordon*, University of California at Santa Barbara

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

We demonstrate a low-cost, tunable, and scalable colloidal lithography method to fabricate suspended TiO₂ high-contrast grating (HCG) reflectors across the visible wavelength range for eventual integration as an output coupler in a resonant-cavity LED. Silica spheres (310-960 nm diameter), deposited via Langmuir-Blodgett dip-coating, were used as a mask to define a quasi-ordered, hexagonal pattern on a 200 nm thick TiO₂ film.

Subsequent pattern transfer with SF₆ reactive ion and XeF₂ chemical etching of sacrificial Si layers beneath the TiO₂ layer yielded a periodic, high index contrast between the suspended array structure and the surrounding air medium. Near-normal-incidence reflectance measurements on structures of increasing hole pitch (310-960 nm) showed an increase in maximum reflected wavelength from 370 to >1000 nm, while maintaining a high-%R bandwidth of 40-100 nm. The reflectance was also observed to be polarization-independent. Finite-difference time domain (FDTD) simulations of structural imperfection stemming from the colloidal lithography process, e.g., deviations in hole diameter, pitch, and hexagonal symmetry, indicate that absolute reflectance is most affected by hole offset from hexagonal lattice positions. The talk will highlight processing methods, optical characterization of HCGs, and underlying trends in the effect of HCG geometry on optical response as predicted by FDTD simulations. This work suggests that scalable fabrication of visible-wavelength HCGs is feasible and holds promise for integration into resonant-cavity LEDs.

11:00am **EM+MI+MN+NS-ThM-10 Nano-optical Activation of Defect-bound Excitons in Monolayer WSe₂: Towards Room-temperature 2D Single-photon Optoelectronics**, *Jim Schuck*, Columbia University **INVITED**

The emergence of two-dimensional (2D) monolayer transition metal dichalcogenides (1L-TMDC) as direct bandgap semiconductors has rapidly accelerated the advancement of room temperature, 2D optoelectronic devices. Optical excitations on the TMDCs manifest from a hierarchy of electrically tunable, Coulombic free-carrier and excitonic many-body phenomena. In our most recent nano-optical investigations of these materials, we have demonstrated that a model hybrid architecture, a nano-optical antenna and a 1L-WSe₂ nanobubble, activates the optical activity of BX states at room temperature and under ambient conditions. These results show that engineered bound-exciton functionality as, in this case, localized nanoscale light sources, can be enabled by an architectural motif that combines localized strain and a nano-optical antenna, laying out a possible path for realizing room-temperature single-photon sources in high-quality 2D semiconductors.

11:40am **EM+MI+MN+NS-ThM-12 Light Scattering Properties of Silver Nanoprisms in Different Environments**, *Yuri Strzhemechny*, Texas Christian University; *S Requena*, Harris Night Vision; *H Doan*, Texas Christian University; *S Raut*, University of North Texas Health Science Center; *Z Gryczynski*, Texas Christian University; *I Gryczynski*, University of North Texas Health Science Center

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

12:00pm **EM+MI+MN+NS-ThM-13 Core-Shell Processing of BTO Nanocomposites for Optimal Dielectric Properties**, *Kimberly Cook-Chennault*, Rutgers University

High permittivity polymer-ceramic nanocomposite dielectric films leverage the ease of flexibility and processing of polymers and functional properties of ceramic fillers. Physical characteristics of these materials can be tuned for application to a variety of applications, such as, advanced embedded energy storage devices for printed wired electrical boards and battery separators. In some cases, the incompatibility of the two constituent materials; hydrophilic ceramic filler and hydrophobic epoxy can limit the filler concentration and therefore, dielectric properties of these materials. Use of surfactants and core-shell processing of composite fillers is traditionally used to achieve electrostatic and steric stabilization for adequate ceramic particle distribution. This work aims to understand the role of surfactant concentration in establishing meaningful interfacial layers between the epoxy and ceramic filler particles by observing particle surface morphology, dielectric permittivity and device dissipation factors. A comprehensive study of nanocomposites that were comprised of non-treated and surface treated barium titanate (BT) embedded within an epoxy matrix was performed. The surface treatments were performed with ethanol and 3-glycidyloxypropyltrimethoxysilan, where the best distribution, highest value of permittivity (~ 48.03) and the lowest value of loss (~0.136) were observed for the samples that were fabricated using 0.5 volume fraction of BaTiO₃ and 0.02 volume fraction of silane coupling agent.

Magnetic Interfaces and Nanostructures Division

Room 203A - Session MI+2D-ThM

Magnetism at the Nanoscale

Moderators: Axel Enders, University of Nebraska-Lincoln, Hendrik Ohldag, SLAC National Accelerator Laboratory

8:20am MI+2D-ThM-2 Magnetic Competition in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Thin Films, **Mikel B. Holcomb**, West Virginia University

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is a strongly correlated ferromagnetic system, commonly proposed for many magnetoresistance applications. Utilizing many techniques (bulk magnetometry, neutron reflectometry and resonant x-ray magnetic scattering), we observe magnetic competition between different magnetic phases in many samples under various growth conditions. This competition results in inverted hysteresis loops (common in superparamagnetic nanoparticles) and negative remanent magnetization. While transmission electron microscopy images show pristine epitaxial growth, the data supports that there are regions of different magnetic order. This results in interesting magnetic measurements, that share similarities with ferrimagnets with competing magnetic lattices. Sample growth and optimization were supported by NSF (DMR-1608656), national facility measurements and theory were supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0016176, and optical measurements by American Chemical Society (PRF #56642-ND10). **We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work.**

8:40am MI+2D-ThM-3 Ferromagnetism in 2D Materials, **Jiabao Yi**, The University of New South Wales, Australia **INVITED**

Discovery of graphene has attracted wide interest of research in the family of 2D layered materials including TMDC (transition metal dichalcogenide), silicene, metal oxide and boron nitride. 2D materials have shown many extraordinary properties, such as high carrier mobility, extra-large mechanical strength and high thermal conductivity and excellent performance in energy storages. Due to its two-dimension nature and high carrier mobility, 2D materials are also very promising for spintronics devices. Graphene has shown long spin diffusion length and high spin injection efficiency [1]. Therefore, introducing magnetism into 2D materials becomes one of the research interests in 2D materials. Doping magnetic element into 2D materials is one of the effective methods to achieve magnetism. Most of the research focuses on theoretical calculations. In this presentation, I will introduce both theoretical calculations and experimental results on magnetic element doped 2D materials. From first principles calculations, it shows defects or defect complexes play important role in the magnetism [2]. In addition, ferromagnetism can be tuned by strain [3]. Experimentally, we observe room temperature ferromagnetism in magnetic element doped 2D materials. Especially, giant coercivity and extremely high magnetization have been observed in magnetic element doped MoS_2 . Defects and shape anisotropy play critical roles in the high magnetization and coercivity [4,5].

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9:20am MI+2D-ThM-5 New Insights into Nanomagnetism by Low-temperature Spin-polarized Scanning Tunneling Microscopy, **Dirk Sander**, Max Planck Institute of Microstructure Physics, Germany **INVITED**

Spin-polarized scanning tunneling microscopy at low temperature (8 K) and in high magnetic fields (6 T) is a powerful technique to investigate magnetic properties of individual nanoscale objects ranging in size from single atoms to several thousand atoms [1]. I focus on the magnetization reversal [2] and the spin-dependent electronic properties of bilayer Co [3], Fe-decorated Co and Fe islands on $\text{Cu}(111)$. We find a novel noncollinear, helical magnetic order in the Fe islands, which is identified by a magnetic stripe contrast with a period of 1.28 nm [4,5] in bilayer islands. The periodicity increases to 2.2 nm in three-layer thick Fe islands [6]. The high spatial resolution of the spin-polarized scanning tunneling spectroscopy in combination with theory reveals the significance of structural and electronic relaxation [7] for the magnetic anisotropy, for subtle balances between ferromagnetic and antiferromagnetic exchange interaction, and

for spin-dependent transport properties [8] of individual, single nanostructures.

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11:00am MI+2D-ThM-10 Materials Optimization to Form Skyrmion and Skyrmion Lattices, **Eric Fullerton**, University of California at San Diego **INVITED**

There is increasing interest in materials systems where magnetic skyrmions can be observed. I will discuss two materials systems where we observe chiral spin structures at room temperature. The first system is ferrimagnetic Fe/Gd-based multilayers where we observe sub-100-nm skyrmions and skyrmion lattices. However, the chirality of the skyrmions are random indicating they are dipole stabilized (similar to of bubble memory in the 1970's) as opposed to by DMI that favors a fixed chirality. This further allows the formation of bi-skyrmions which result from the merging of two skyrmions of opposite chirality and anti-skyrmions. We find that there is a transition from stripe domains to a skyrmion lattice and then individual skyrmions with magnetic fields and this behavior is sensitive to alloy composition, film thickness, temperature, and field history and only emerges in a narrow range of parameters. Using micromagnetic modeling we are able to quantitatively reproduce our experimental observations. The modeling suggests that the domain wall is Bloch-like in the center of the films but broadens and transitions to more Néel-like towards the surface forming closure domains. The Bloch-like centers have an equal population of the two helicities while the Néel-like part of the walls will have the same helicity at the top of the film and the opposite helicity at the bottom of the film which allows coupling to spin-orbit-torque layers. The second system is Pt/Co(1.1 nm)/Os(0.2 nm)/Pt heterostructures. Using Kerr microscopy to observe skyrmions for a narrow temperature and field range. With relatively low currents, it is possible to generate and move these skyrmions both within patterned wires and full films and we further have observations of the skyrmion Hall effect. The research is done in collaboration with S. A. Montoya, R. Tolley, J. Brock, S. Couture, J. J. Chess, J. C. T Lee, N. Kent, D. Henze, M.-Y. Im, S.D. Kevan, P. Fischer, B. J. McMorran, V. Lomakin, and S. Roy and is supported by the DOE.

11:40am MI+2D-ThM-12 Giant Magnetostriction and Low Loss in FeGa/NiFe Nanolaminates for Strain-Mediated Multiferroic Micro-Antenna Applications, **Kevin Fitzell**, *C Rementer*, University of California, Los Angeles; *N Virushabadoss*, University of Texas at Dallas; *M Jamer*, National Institute of Standards and Technology (NIST); *A Barra*, University of California, Los Angeles; *J Borchers*, *B Kirby*, National Institute of Standards and Technology (NIST); *G Carman*, University of California, Los Angeles; *R Henderson*, University of Texas at Dallas; *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 low-loss magnetic material with strong magnetoelastic coupling at high frequency.

¹ Falicov Student Award Finalist

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Galfenol ($\text{Fe}_{84}\text{Ga}_{16}$ or FeGa) is a promising candidate material due to its large magnetostriction (>200 ppm), large piezomagnetic coefficient (>3 ppm/Oe), and high stiffness (>50 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 (ferromagnetic resonance linewidth <20 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. Optimized magnetic laminates were shown to exhibit a small coercive field (<20 Oe), narrow ferromagnetic resonance linewidth (<40 Oe), and high relative permeability (>400) (Rementer et al., 2017). In addition, optical magnetoelastic measurements of these laminates confirmed the presence of strong magnetostriction; relative to single-phase FeGa, these laminates represent a threefold enhancement in magnetostriction at saturation and up to a tenfold enhancement at low magnetic fields.

Multiferroic composites incorporating these magnetic laminates were then studied via polarized neutron reflectometry, demonstrating coherent rotation of the individual layers' magnetization with an applied electric field across distances much larger than the exchange length of either material. Micromagnetic and finite element simulations support the experimental results, showing coherent rotation of the magnetization with only small deviations with thicker NiFe layers. Subsequent integration of these laminates into strain-mediated multiferroic antennae confirmed the absorption of electromagnetic and acoustic waves, showing great promise for the use of FeGa/NiFe laminates in micro-scale communications systems.

12:00pm **MI+2D-ThM-13 Structural and Electronic Origin of Stable Perpendicular Magnetic Anisotropy in Pt/Co/Pt magnetic ultra-thin film with Ti Buffer Layer**, *Baha Sakar*, Gebze Technical University, Turkey; *Z Balogh-Michels, A Neels*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *O Öztürk*, Gebze Technical University, Turkey

In this work, Pt and Co based multilayer samples with perpendicular magnetic anisotropy (PMA) are prepared. The aim of the work is the optimization and stabilization of the magnetic properties. Highly stable and repeatable PMA samples are demanded for standardization and calibration of magnetic measurements. For this purpose, Pt/Co/Pt (pcp) and Ti/Pt/Co/Pt (tpcp) samples are prepared on naturally oxidized Si(111) substrates by using magnetron sputtering. Electronic structures and elemental composition of the sample surfaces are investigated by X-Ray Photoelectron Spectroscopy. The same technique is also used for thickness calibrations of depositions. Magnetic properties of the samples are investigated by using Magneto-Optical Kerr Effect method. Orientations of the grains are important for defining the magnetic easy axis of a magnetic material. Typical symmetric XRD scans are not suitable for very thin films (<10 nm) since the signal to background ratio is low. For this reason, structural properties of the films are analyzed by using grazing angle XRD and in-plane XRD reciprocal space mapping.

Samples with the titanium buffer layer (tpcp) have perpendicular magnetic anisotropy where the pcp samples have in-plane magnetization. Structural differences in the presence of Ti layer are the strong preferred orientation for Pt, while the pcp film is random oriented. Multiple Co reflections are also visible for the pcp film. These confirmed a 111 fiber texture for the Pt in case of the tpcp sample. Contrary to that multiple Pt rings are observed for the pcp sample, which agrees with a random oriented nanocrystalline film. The lack of a texture explains the magnetic behavior.

Samples prepared in this work are used/using and studied within a joint research project, EMPiR SIB05 NanoMag funded by EURAMET.

Nanometer-scale Science and Technology Division

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

Nanopatterning and Nanofabrication

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

8:00am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-1 Femtosecond Laser Processing of Ceria-Based Micro Actuators**, *Jenny Shklovsky*, Tel Aviv University, Israel; *E Mishuk*, Weizmann Institute of Science, Israel; *Y Berg*, Orbotech Ltd, Israel; *N Vengerovsky*, *Y Sverdlov*, Tel Aviv University, Israel; *I Lubomirsky*, Weizmann Institute of Science, Israel; *Z Kotler*, Orbotech Ltd; *S Krylov*, *Y Shacham-Diamond*, Tel Aviv University, Israel

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

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

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

*Three first authors contributed equally to this abstract.

8:20am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-2 Synthesis of Functional Particles by Condensation and Polymerization of Monomer Droplets in Silicone Oils**, *Prathamesh Karandikar*, *M Gupta*, University of Southern California

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

The viscosity of the silicone oil was systematically varied from 100 cSt through 100,000 cSt. A heterogeneous particle size distribution was produced at low viscosities of silicone oil where the smaller particles were formed by the cloaking and engulfment of monomer droplets nucleated at the vapor-liquid interface and the larger particles were formed by coalescence inside the liquid. Coalescence could be inhibited by increasing the viscosity of the silicone oil leading to a decreased average radius and a narrower size distribution of the polymer particles. A transition to polymer film formation was observed for the 100,000 cSt silicone oil substrates. We

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studied the polymerization of two different monomers, 4-vinyl pyridine and 2-hydroxyethyl methacrylate, since these polymers have a variety of useful properties such as pH-responsiveness and biocompatibility. Our process enables fabrication of functional particles with average diameters ranging from 100 nm – 500 nm with fast reaction times (\approx 15 min). The advantages of our method for the fabrication of polymer particles are that it does not require surfactants or organic solvents and features short reaction times compared to conventional polymer particle synthesis methods such as emulsion polymerization.

8:40am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-3 Competition Between Scale and Perfection in Self-assembling Structures, James Liddle**, NIST Center for Nanoscale Science and Technology **INVITED**

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

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

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

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9:20am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-5 Polymer Templated Annealing of DNA Patterned Gold Nanowires, Tyler Westover, B Aryal, R Davis, A Woolley, J Harb**, Brigham Young University

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

Electrical contacts to the randomly oriented 400 nm long wires were made by electron beam induced deposition. Nanowire morphology was measured before and after annealing by scanning electron and high resolution transmission electron microscopy.

11:00am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-10 Directed Self-assembly of Block Copolymers for Applications in Nanolithography, Paul Nealey**, University of Chicago **INVITED**

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

11:40am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-12 Three Dimensional Mesoporous Silicon Nanowire Network Fabricated by Metal-Assisted Chemical Etching, Deepak Ganta, C Guzman, R Villanueva**, TAMIU

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

To address the problem, we report a simple and inexpensive method of fabricating 3D mesoporous Si nanowire network by metal-assisted chemical etching (MacEtch). Degenerately doped p-type silicon or p+ silicon wafer (0.001 \sim 0.005 Ω -cm) was coated with about 22 nm silver film at 350 °C for 5~6 hours in a vacuum furnace (pressure < 3 \times 10⁻⁷ Torr). Scattered silver particles with different sizes were formed as a result of the dewetting process. Then we deposited 10~11 nm of noble metal (Au) at 0.5 Å/s rate, followed by silver lift-off to obtain an Au mesh as an etching mask. The mixture of a chemical solution of HF: H₂O₂: Ethanol = 30:1:1 is used as a chemical etchant under room temperature. The time of immersion of the silicon wafer in the etchant effects the aspect ratio of the silicon nanowire array. After MachEtch, the Au is removed by immersing the sample in the aqua regia solution. The ratio of the chemicals in the etchant will affect the pore size. The aspect ratio of the silicon nanowire network can be controlled by the etching rate. The etching rate was roughly one μ m/min. The 3D network is formed as the length of the 1D silicon nanowires (50 nm -100 nm) was varied, followed by critical point drying to carefully control the uniformity of 3D silicon nanowire network on the entire surface area of the 6-inch silicon wafer.

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

12:00pm **NS+AN+EM+MI+MN+MP+PS+RM-ThM-13 Enhancing Light Extraction from Free-standing InGaN/GaN light Emitters Using Bio-inspired Backside Surface Structuring, L Chan, C Pynn, S DenBaars, Michael Gordon**, University of California at Santa Barbara

A simple, scalable, and reproducible nanopatterning method to create close-packed (moth-eye like) patterns of conical nano- and microscale features on InGaN/GaN LED surfaces, and on the backside outcoupling surface of LED devices, is presented. Colloidal lithography via Langmuir-Blodgett dip-coating using silica masks (d = 170–2530 nm) and Cl₂/N₂-based

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

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 202A - Session SA+MI-ThM

Ultra-fast Dynamics for Magnetic and Quantum Systems

Moderator: Claus Michael Schneider, Forschungszentrum Juelich GmbH, Germany

8:00am SA+MI-ThM-1 New Opportunities at the APS: Using Intermediate Energy X-rays to Investigate Collective Behavior in Interacting Electron Systems, *Jessica McChesney, F Rodolakis*, Argonne National Laboratory

In an effort to address one of the grand challenges for condensed matter physics in the 21st century, namely to gain an understanding of the physics of materials which exhibit collective electronic phenomena, the Advanced Photon Source has developed the intermediate-energy x-ray (IEX) beamline. Now fully operational, this beamline enables the investigation of collective behavior in interacting electron systems using two distinct but complementary techniques: angle-resolved photoemission spectroscopy and resonant soft x-ray scattering. In this talk, I will discuss some of the unique capabilities of the beamline and present several examples of collective behavior in interacting electron systems including electron-phonon coupling, spin and charge density waves and orbital ordering in high-temperature superconductors, transition metal oxides, topological insulators and heavy fermion materials.

8:20am SA+MI-ThM-2 Observation of Surface Recombination in Ultra-fast Carrier Dynamics of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Thin Films, *Saeed Yousefi Sarraf, G Cabrera, R Trappen, N Mottaghi, S Kumari, C Huang, A Bristow, M Holcomb*, West Virginia University

Perovskite oxides (ABO_3) are a promising class of transition metal oxides that have attracted significant attention in material science due to diverse range of properties. Many studies on structural and magnetic properties have been done on perovskite oxides to base the multifunctional devices made by and proposed for these materials. Yet another very important property of perovskite oxides is that many of their band gaps are in the visible range. These gaps make these oxides a suitable choice for photovoltaic applications. However, despite the very critical role this property plays in light harvesting devices, there has been a limited understanding about the carrier dynamics of these materials, which inform us about the efficiencies of photovoltaic devices, especially in lower thicknesses. Since by decreasing the film thickness, the surface to bulk ratio increases and surface electrons dominate the bulk electrons, surface recombination might occur as an extra channel of energy relaxation, which decreases the device efficiency. Perovskite oxide $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) thin films were fabricated with different thicknesses by pulsed laser deposition on (100) SrTiO_3 single crystal substrates. Our films' quality were checked by in situ RHEED patterns and oscillations, X-ray diffraction and reflectivity, magnetometry and atomic force microscopy. Ultra-fast carrier dynamics were studied by a degenerate reflectivity pump probe setup at 800nm for different film thicknesses and different pump powers. For films with a

thickness above $\sim 20\text{nm}$ three different recombination were observed, attributed to electron phonon relaxation, spin lattice phonon relaxation and thermal diffusion relaxation. However, for films thinner than $\sim 20\text{nm}$ an extra relaxation mechanism was observed, which we attributed to surface recombination. This optics work was funded by the American Chemical Society (PRF #56642-ND10); sample growth and optimization were supported by NSF (DMR-1608656).

8:40am SA+MI-ThM-3 Non-equilibrium Control of Charge & Spin Motion in Quantum Materials, *Hermann Dürr*, Uppsala University, Sweden INVITED

A key driver of modern information technology is the quest for "smaller and faster" information processing and storage. The ultimate speed limit is the speed of light. Therefore, the idea to probe, change and control properties of materials with the help of light has long intrigued researchers in materials science. Of particular interest are magnetic materials which in nanostructured form are used for data storage, memory and processing. In this talk I will show several examples the unique potential of using femtosecond soft x-ray pulses from x-ray free electron lasers such as the LCLS to probe in real time ultrafast spin dynamics in nanoscale systems and during all-optical magnetic switching. Understanding and ultimately engineering the evolving electron, spin and lattice motion on the time- and lengthscales associated with the relevant interactions promises new ways for storing and processing of information.

9:20am SA+MI-ThM-5 XUV-transient Grating: Probing Fundamental Excitations at the Nanoscale, *Laura Foglia, F Capotondi, R Mincigrucci, D Naumenko, E Pedersoli, A Simoncig, G Kurdi, M Manfreda, L Raimondi*, Elettra-Sincrotrone Trieste, Italy; *N Mahne*, IOM-CNR, Italy; *M Zangrando, C Masciovecchio, F Bencivenga*, Elettra-Sincrotrone Trieste, Italy INVITED

Nonlinear optical spectroscopies take advantage of multiple light-matter interactions via the Nth-order susceptibilities, to disentangle and selectively access the many interacting degrees of freedom that characterize complex systems. Indeed, the control on photon parameters (frequency, arrival time, polarization, etc.) for each field independently gives rise to a manifold of experimental techniques that allow to monitor, on ultrafast timescales, structural changes, spin and electron dynamics, collective phenomena as well as to selectively probe correlations among different excitations. Among the nonlinear processes, third order, or four-wave-mixing (FWM), interactions occur in all materials independently of their symmetry, and are thus the most widely used in applications. While nowadays these techniques are well established at optical wavelengths, their birth required the invention of the laser. Similarly, their extension to sub-optical wavelengths (XUV and X-ray), envisioned theoretically more than a decade ago, had to wait until the recent development of free electron lasers (FELs). XUV-FWM will allow exploiting core-hole resonances to address correlations among low-energy excitations and core states as well as monitoring charge and energy transfer processes. Additionally, it will extend the accessible wavevector range to the mesoscopic regime ($0.1-1\text{ nm}^{-1}$), which is fundamental to investigate, e.g., lattice dynamics in nanostructures and disordered systems as well as transport phenomena at the nanoscale.

Here I report on the demonstration of XUV four-wave-mixing response in a transient grating (TG) approach, exploiting the unique properties of the seeded FEL source FERMI and of two dedicated setups: TIMER and mini-TIMER. All-XUV TG data allowed us to determine the phonon and thermal dynamics of several semiconductors in an uncharted length-scale range, extending down to $\approx 20\text{ nm}$. The results are compared with those of XUV pump/optical probe TG, evidencing different couplings to the electronic subsystem.

Additionally, I present the first evidence of FWM processes stimulated by FEL pulses at different wavelengths, obtained exploiting the multi-color capabilities of FERMI and will discuss the foreseen implementation of second order wave-mixing techniques for the chemical and interface specific probing of electronic processes.

11:00am SA+MI-ThM-10 Study of Photo-induced Dynamics in Quantum Materials using Femtosecond Time-resolved X-ray Scattering, *Wei-Sheng Lee*, SLAC National Accelerator Laboratory INVITED

It remains a great challenge to characterize and understand photo-induced dynamics in quantum materials when it is driven out-of-equilibrium by ultrafast photon pulses. Time-resolved x-ray scattering, enabled by x-ray free electron laser, can track the time-evolution of the magnetic, charge, and lattice degrees of freedom with femtosecond time resolution, providing new insights into the photo-induced dynamics. In this presentation, I will first highlight photo-induced dynamics of spin and

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charge orders in striped nickelate. The strong coupling between spin and charge orders still survives, despite that both orders have been strongly suppressed by photo-excitations [1,2]. In addition, by resonantly pumping a bond-stretching phonon using mid-IR pulses, we observed lattice-driven dynamics that is different from hot-electron-driven dynamics induced by optical pumping across the band gap [3]. Then, I will discuss phenomena associated with coherent lattice oscillations by highlighting the measurement of atomic displacement of a coherent A1g mode in an iron-based superconductor BaFe₂As₂, which can be correlated with accompanied electronic variations [4]. In particular, a quantitative “lock-in” comparison between electronic band structure obtained by time-resolved ARPES and the measured atomic displacements allows us to directly obtain orbital-specific electron-phonon coupling strength without any prior assumption of the electronic band structures [5]. Finally, I will showcase a proof-of-principle time-resolved RIXS experiment on CDW ordered 1T-TiSe₂ as an outlook for the future time-resolved x-ray scattering experiment in the next generation x-ray free electron laser, such as the LCLS-II.

1. W. S. Lee et al., Phase fluctuations and the absence of topological defects in photo-excited charge ordered nickelate. *Nature Communications* 3, 838 (2012).
2. Y. D. Chuang, W. S. Lee et al., Real-Time Manifestation of Strongly Coupled Spin and Charge Order Parameters in Stripe-Ordered La_{1.75}Sr_{0.25}NiO₄ Nickelate Crystals Using Time-Resolved Resonant X-Ray Diffraction. *Phys. Rev. Lett.* 110, 127404 (2013).
3. W. S. Lee et al., Non-equilibrium Lattice-driven Dynamics of Stripes in Nickelates using Time-Resolved X-ray Scattering. *Phys. Rev. B* 95, 121105(R) (2017).
4. S. Gerber, et al., Direct characterization of photo-induced lattice dynamics in BaFe₂As₂. *Nature Communication* 6, 7377 (2015).
5. S. Gerber, S.-L. Yang et al., Femtosecond electron-phonon lock-in via photoemission and x-ray free-electron laser. *Science* 357, 71 (2017).

11:40am **SA+MI-ThM-12 HAXPES Lab- A Home Lab System for HAXPES Measurements**, *S Eriksson*, Scienta Omicron; **Anna Regoutz**, Imperial College London, UK

During the past decade, increased attention has been shown to hard X-rays in the photoelectron spectroscopy field. This is mainly due to the increased information depth enabled by the higher photon energies. Such bulk sensitive measurements could previously only be performed at dedicated synchrotron radiation facilities. The beam lines providing this type of radiation are heavily booked, so access to the experimental setups is thus limited. Higher excitation energies also enables bulk sensitive measurements of deep core levels not accessible with standard XPS.

Here we present a new product featuring a monochromized X-ray source giving out Ga Ka radiation at 9.25keV and a wide acceptance angle hemispherical electron analyzer, both combined on a simple to use vacuum system. The base system can easily be customized by adding separate modules such as a MBE- or preparation chamber or a glove box. With this system, a new set of possible experiments opens up in the home laboratory: investigations of buried interfaces, in operando devices, real world samples, etc.

The X-ray source consists of a MetalJet X-ray tube and the electrons which are accelerated into this jet generate an intense Ga Ka radiation. These X-rays are monochromized using a newly developed monochromator. The small spot size of 20 μm provided by the liquid jet source is maintained throughout the passing of the monochromator and only slightly broadened to about 50μm. In order to allow for easy adjustment of the X-ray focal point relative to the electron analyzer, the entire assembly of monochromator and source can be moved down to a precision of a few micrometers. The hemispherical electron analyzer is configured for high kinetic energies allowing for detection of the full energy range the source provides and a large acceptance angle of +/- 30 degrees. The overall system resolution is shown to be <0.5 eV.

We present data taken from polycrystalline gold and silicon wafers with a surface layer of silicon dioxide with a controlled thickness as well as transistor stacks and energy related materials.

Magnetic Interfaces and Nanostructures Division Room 203A - Session MI+BI-ThA

Interdisciplinary Magnetism

Moderator: Markus Donath, Muenster University, Germany

2:40pm MI+BI-ThA-2 Chiral Induced Spin Selectivity in Molecular Bond Dissociation, **Richard Rosenberg**, Argonne National Laboratory

Since nearly all biological compounds are homochiral, any model of the origin of life must be able to incorporate a mechanism that could lead to preferential chirality. Since chiral molecules have a certain handedness, many researchers have investigated the possible influence of circularly polarized UV photons and longitudinal spin-polarized electrons in creating an enantiomeric excess.[1-3] However, in general the demonstrated effects have been small and/or on the order of the experimental error. Previously we demonstrated [4] that chiral-selective chemistry occurs when X-rays irradiate a chiral molecule bound to a magnetic substrate and suggested that a previously unappreciated source may play a role in chiral-selective chemistry: low-energy (0-20 eV) spin-polarized secondary electrons, produced by photon, electron, or ion irradiation. In the present work, we explore a possible alternative mechanism based on the chiral induced spin selectivity (CISS) effect [5] which suggests that the lifetime of an excited electron in a chiral molecule bound to a magnetic substrate should depend on the magnetization direction of the substrate. To investigate this possibility, we examined the photon-stimulated desorption yield of hydrogen ions from D- and L-Histidine bound to a magnetized cobalt film. The data indicates differences in the N K edge spectra of the H⁺ ion yield depending on the substrate magnetization direction. These results suggest a possible CISS effect on the excited state lifetime of the dissociative state. Such a mechanism would be applicable to any process that leads to an excited electron in a dissociative state of a chiral molecule bound to a magnetic substrate. Iron is one of the most common elements and many iron compounds are magnetic, so such a mechanism could be applicable in a wide range of prebiotic environments.

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3:00pm MI+BI-ThA-3 The Chiral Induced Spin Selectivity Effect- From Spintronics to Controlling Chemistry, **Ron Naaman**, Weizmann Institute of Science, Israel **INVITED**

Spin based properties, applications, and devices are commonly related to magnetic effects and to magnetic materials. However, we found that chiral organic molecules can act as spin filters for photoelectrons transmission, [i] in electron transfer, [ii] and in electron transport. [iii]

The new effect, termed Chiral Induced Spin Selectivity (CISS), [iv] enables new type of spintronics, [v] has interesting implications in Biology, [vi] varying from allowing long-range electron transfer, controlling multiple electrons reactions, and in enantio-recognition.

The effect and its various applications and implications will be discussed.

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4:00pm MI+BI-ThA-6 Multifunctional Ferromagnetic Disks for Life Sciences Applications, **Elena Rozhkova**, V Novosad, Argonne National Laboratory **INVITED**

The impact of modern nanomaterials and engineered architectures on biological modulation, bioanalytical techniques, and healthcare technologies can hardly be overestimated. Magnetic nanomaterials are attractive for life sciences applications because they can be detected and operated remotely, biological barriers-free, using external magnetic field. Using top-down micro-/nano-fabrication techniques allows for production of monodisperse magnetic particles of virtually any composition and shape, with tunable magnetic properties. Such particles have been exploited as multi-spectral MRI contrast enhancement labels, for *in vitro* detection of molecular markers and cell sorting. This talk will summarize successful applications of lithographically defined disk-shaped particles composed of ferromagnetic Fe₂₀Ni₈₀ permalloy core for biomedical applications in both low- and high frequency magnetic field regimes as mediators of biological mechanotransduction, as delivery vehicles, contrast agents and ultrasensitive detection labels. Advanced synchrotron imaging was used to visualize interaction of engineered nanomagnetic hybrids with living systems and study their chemical stability at subcellular, cellular and 3D multicellular levels.

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4:40pm MI+BI-ThA-8 Magnetic Nanoparticles in Biomedicine: Recent Developments in Imaging, Diagnostics and Therapy, **Kannan Krishnan**, University of Washington **INVITED**

The Néel relaxation of magnetic nanoparticles (MNP), subject to alternating magnetic fields in solution, depends exponentially on their core diameter while the complementary Brownian relaxation mechanism depends critically on their hydrodynamic volume [1]. Recent developments [2] in the synthesis of highly monodisperse and phase-pure magnetite nanoparticles allows for reproducible control of the former in biological environments, enabling novel imaging [3,4] and spectroscopic modalities, under ac excitations such as magnetic particle imaging/spectroscopy (MPI/MPS) with superior resolution and sensitivity [5]. [8]

Magnetic Particle Imaging (MPI) is an emerging, tracer-based, whole-body medical imaging technology with high image contrast (no tissue background) and sensitivity (~250 nm Fe) to an optimized tracer consisting of an iron-oxide nanoparticle core and a biofunctionalized shell. MPI is linearly quantitative with tracer concentration and has zero tissue depth attenuation. MPI is also safe, uses no ionizing radiation and clinically approved tracers. MPI is also the first biomedical imaging technique that truly depends on nanoscale materials properties; in particular, their response to alternating magnetic fields in a true biological environment needs to be optimized.

In this talk, I will introduce the underlying physics of MPI, the alternative approaches to image reconstruction, and describe recent results in the development of our highly optimized and functionalized nanoparticle tracers for MPI. I will then present state-of-the-art imaging results of preclinical *in vivo* MPI experiments of cardiovascular (blood-pool) imaging [6], stroke [7], GI bleeding [8], and cancer [9] using rodent models. I will also discuss a related diagnostic method using magnetic relaxation and illustrate its use for detecting specific protease cancer markers in solution [10]. If time permits, I will introduce therapeutic applications of magnetic nanoparticles [11].

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Surface Science Division

Room 203C - Session SS+AS+BI+MI+NS-ThA

Organic/Inorganic Surfaces, Interfaces and Nanostructures

Moderator: Denis Potapenko, Princeton University

2:20pm **SS+AS+BI+MI+NS-ThA-1 Investigation of the Stability of Ag Monolayers on Au(111) as a Function of Metal Adatom Diffusion**, J Phillips, L Harville, H Morgan, L Jackson, G LeBlanc, Erin Iski, University of Tulsa

The formation of an atomically thin, Ag layer on a Au(111) surface has been shown to significantly alter the thermal properties of the underlying substrate (1). A further exploration into the chemical mechanisms by which these thin films are deposited reveals two different sources of Ag during the formation of the monolayer. Electrochemical Scanning Tunneling Microscopy (EC-STM) and Cyclic Voltammetry (CV) are used to probe the *in-situ* interfaces of these metal systems as well as the adsorption of molecules on metals. EC-STM is a unique technique that, in addition to providing a local probe of the atomic surface structure, also functions as a 3-electrode cell in which redox chemistry can be performed to understand the chemical reactivity of the surface. Also, cyclic voltammograms (CVs) can be generated to provide specific information regarding the nature of the redox events occurring at the surface. The two sources of silver used for the Underpotential Deposition (UPD) process on Au(111) result in significantly different thermal stabilities of the surface. An important question is whether this stability can extend beyond thermal properties, which will be probed using the assembly of amino acids on Ag/Au(111). Using both EC-STM and UHV-STM (ultra-high vacuum STM), it has been shown that amino acids assist in the immobilization of diffusing adatoms on the surface and in the subsequent formation of metal islands (2). Since the molecular deposition in both cases takes place at room temperature, the current understanding is that the atoms on the surface are a function of the temperature of the surface and are not pulled out of the surface itself. Importantly, these systems provide a unique glimpse into metal surface diffusion and offer the ability to study the mass transport of metal atoms. This study focuses on how an application of the thin Ag film on the Au(111) will disrupt or assist in the metal adatom transport and whether the known thermal stability can extend to other surface properties, thus making the afforded stability more general. The interaction of the amino acids with the Ag films deposited at the two different potentials and the associated mass transport as measured by the size of metal islands on the surface will shed light on the stabilities of the two types of Ag layers. The ability to experimentally choose different surface properties based on electrochemical parameters and solution composition during metal deposition could lead to exciting new directions for thin film technologies.

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(2) Iski et al. *submitted to Communication Chemistry*, May 2018.

2:40pm **SS+AS+BI+MI+NS-ThA-2 Chain-Length Dependent Reactivity of Thiolate Self-Assembled Monolayers with Atomic Gas Species**, Jeffrey Sayler, S Brown, S Sibener, University of Chicago

Thiolate self-assembled monolayers (SAMs) provide platforms for easily customizable organic interfaces, making them an excellent model system for studying the chemical properties of organic thin films. In particular, their reactions with atomic gas species such as hydrogen and oxygen yield important information about gas-surface interactions in organic films, how static and dynamic disorder influence passivation, as well as various hydrogenation and oxidation reactions. We are currently investigating the reactions of these SAMs with atomic hydrogen (H), using an angle-directed atomic gas source and *in situ* ultra-high vacuum scanning tunneling microscopy (UHV-STM). First, a series of alkanethiolate SAM samples of

varying chain length (8 to 11 carbon atoms long) were reacted with H, resulting in the monolayers' conversion from close-packed standing-up phase to lower density lying-down phase. Regardless of chain length or even/oddness, which were expected to impact the effectiveness of H penetration into the monolayer due to differences in the chains' lateral mobility and terminal structure, all samples exhibited common kinetic mechanistic details. The relative reaction rates of different chain lengths were obtained using simultaneous dosing of multiple samples. Second, a close-packed 1H,1H,2H,2H-perfluorodecanethiol SAM (a fluorinated analog of the 1-decanethiol SAM) was reacted with H. Dosing this sample under the same conditions as the 1-decanethiol sample revealed little to no reactivity. Ongoing studies continue to explore the reactivity of this family of saturated SAM systems including investigation of the kinetics and mechanism of the lying-down phase's reactivity with H. Further investigations involving atomic oxygen and different SAM chemical compositions and structures will follow.

3:00pm **SS+AS+BI+MI+NS-ThA-3 Scan Probe Studies of Lithium Transfer through Solid State Electrochemical Interfaces**, Janice Reutt-Robey, University of Maryland College Park

INVITED

All solid-state electrical energy storage devices are of immense interest as safer alternatives to those based upon flammable liquid electrolytes. Understanding the rates and elementary processes for lithium ion transport through anode-solid electrolyte-cathode interfaces is essential, but obscured by heterogeneous samples and unknown local potentials. I will present new nanoscale studies of lithiation/delithiation across well-defined interfaces created with actuated nanobattery junctions. Conventional STM metallic tips, clad with a thin film of electrode material (LiCoO₂ or Li) and a capping film of solid electrolyte (Li_xAl₂O₃ or Li₂O), function as ½ cells. Probes are positioned and electrochemically cycled at singular surfaces of model electrodes – Si(111), Si(100), C(0001). At the nanoscale, hysteresis in charging/discharging is monitored as a function of interface structure and materials properties. UHV measurements preserve the chemical integrity of the material interfaces and allow traditional (cyclic voltammetry, stepped potential) and nontraditional (stepped stress) electrochemical measurements to separate electron/ion contributions to charge transfer. The data reveal how induced variations in local lithium concentration impact rates for charging/discharging and contribute to hysteretic behavior. Further, stress-induced current transients show non-Cotrellian time behavior, attributed to a lithium ion concentration gradient in the solid electrolyte. Modeling of nanobattery data allows for testable predictions of material properties. Finally we show how "inverted" Scanning Tunneling Spectroscopy provides a useful tool to characterize the electrical band gap of the tip 1/2 cell materials, while imaging reveals the distribution pattern of lithium ions at the cycled electrode surfaces.

This work was supported as part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award number DESC0001160.

4:00pm **SS+AS+BI+MI+NS-ThA-6 Adsorption and Self-assembly of Halogenated Organic Molecules on the Si(111) √3×√3-Ag Surface**, Renjie Liu, Lakehead University, Canada; C Fu, A Moiseev, M Rao, Y Chen, D Perepichka, McGill University, Canada; M Gallagher, Lakehead University, Canada

Given potential applications in molecular electronics, organic thin films continue to attract a great deal of scientific attention. Furthermore, organic-inorganic semiconductor hybrids have been identified as a possible platform for future devices. Generally such a device would require thin films of functionalized organic molecules grown on silicon surfaces. To promote the growth of high quality films, the Si surface needs to be passivated. For example, the Si(111) √3×√3-Ag surface has been shown to be weakly interacting, allowing molecules to remain mobile and form well ordered layers [1].

In this work we compare the adsorption and self-assembly of two halogenated molecules of threefold symmetry; 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (TIPT), and tribromotrioxaazatriangulene (TBTANG) on the Si(111)-√3×√3-Ag surface. The self assembly of TIPT on HOPG and Au(111) has been reported previously [2], and heteroatom forms of triangulene are of particular interest in molecular electronics [3].

We find that both molecules display high mobility on the √3-Ag surface. With increasing molecular dose, TIPT forms supramolecular domains defined by a 2.0 nm by 1.8 nm rectangular cell. The size and symmetry of the unit cell provides strong evidence that a large fraction of the monomers do not undergo de-halogenation, and that the dominant

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interaction within the domains is intermolecular I...H hydrogen-bonding. As the coverage approaches one monolayer, the film consists of supramolecular domains of limited extent separated by regions of disorder. STM images at lower coverage reveal that molecular adsorption increases the defect density of the underlying $\sqrt{3}$ -Ag layer. We believe that a small fraction of the TIPT molecules de-iodinate on adsorption and that the iodine subsequently reacts with the Ag overlayer. The increased defect density limits the extent of the supramolecular domains on this surface.

In contrast, TBTANG exhibits long-range self-assembly of intact molecules. The ordered structure is characterized by several closely packed rows of molecules. Within the rows the repeating motif is two-molecules linked together by Br...Br interactions. With increasing coverage, the $\sqrt{3}$ surface remains unaffected and the self assembled layer extends over the entire surface.

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[2] Gatti, R. *et al.*, *J. Phys. Chem. C* **118**, 25505–25516 (2014).
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4:20pm SS+AS+BI+MI+NS-ThA-7 Electron Interactions with Alkanethiol Self-assembled Monolayers on Au(111), Jodi Grzeskowiak, University at Albany-SUNY; C Ventrice, Jr., SUNY Polytechnic Institute

Self-assembled monolayers (SAMs) are often used for applications such as molecular electronics, selective deposition, and various forms of surface modification. Advanced lithography within the semiconductor industry is adopting ever shorter wavelengths of light such that the interaction of secondary electrons with the organic resist is becoming the primary mechanism for photo-initiated electro-chemical solubility changing reactions. In order to study the interaction of low energy electrons with thin organic films, measurements have been performed on electron decomposition of alkanethiol molecules grown on Au(111) substrates. SAMs have been grown via both solution and vapor phase methods. These monolayers arrange into two distinct phases commonly referred to as lying down and standing up. The lying down phase is a physisorbed layer that is only weakly interacting with the substrate via Van der Waals forces. Conversely, the standing up phase is a chemisorbed species that is more strongly bound to the substrate. Various surface analysis techniques were used to characterize the monolayers before and after electron exposure. Low energy electron diffraction (LEED) was used to determine the structure of the SAM and the rate of decomposition. Temperature programmed desorption (TPD) in combination with mass spectrometry was used to evaluate the thermal stability and bonding strength of the attached SAMs and the decomposition products from electron exposure.

4:40pm SS+AS+BI+MI+NS-ThA-8 Measuring the Electronic Properties of Organic Single Crystals, Sujitra Pookpanratana, E Bittle, C Hacker, S Robey, National Institute of Standards and Technology (NIST); R Ovsyannikov, E Giangrisostomi, Helmholtz-Zentrum Berlin, Germany

Organic and molecular-based compounds have found commercial application in consumer-based electronics. Organic semiconductors can be integrated onto device structures in different physical forms such as single crystals, polycrystalline thin-films, or amorphous thin-films. The structural order of the molecular solid profoundly influences the electronic properties, that in turn controls important properties, such as the transport gap and binding energy of the highest occupied molecular orbital (HOMO) [1, 2], that govern how an electronic device operates. Photoemission can play a vital role in illuminating these important electronic properties. While there are numerous photoemission spectroscopic measurements of organic semiconductors in thin-film structures, far fewer attempts have been made to determine the “fundamental” electronic properties for pristine organic single crystals.

Here, we present results of photoemission measurements for single crystalline (SC) dinaphthothienothiophene (DNNT). DNNT is a small molecule-based thienoacene and has demonstrated carrier mobilities approaching $10 \text{ cm}^2/(\text{V s})$ [3], is air-stable [4] and durable against accelerated temperatures and humidity conditions.[5] While there are many device studies that establish DNNT and other related thienoacenes for a variety of applications, detailed electronic and chemical structure studies are lacking. Electronic “band” structure measurements using a novel angle-resolved time-of-flight electron spectrometer is performed on SC-DNNT, and multiple highest occupied molecular orbitals are resolved of varying widths. Modest dispersion of the frontier HOMO is observed, and

this result will be discussed in context of the charge carrier behavior of DNNT reported in the literature.

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5:00pm SS+AS+BI+MI+NS-ThA-9 Surface Functionalization of Porous Substrates via Initiated Chemical Vapor Deposition, Christine Cheng, M Gupta, University of Southern California

Porous materials are used in various applications including separation membranes, paper-based microfluidics, and flexible electronics. Tuning surface properties of porous materials enhances the versatility of existing materials, giving them new functions and applications. However, traditional surface modification methods are typically solvent-based, which limits the range of substrates that can be coated. In this work, initiated chemical vapor deposition was used to continuously modify the surface of large areas of porous substrates in an all-dry vacuum process. A superhydrophobic polymer was deposited onto a porous substrate and the coating was characterized using contact angle goniometry, X-ray photoelectron spectroscopy, and scanning electron microscopy to study the uniformity of the coating along the entirety of the substrate. The superhydrophobicity of the coated porous substrate is attributed to the deposited polymer and the roughness of the substrate. Addition of a perfluorinated liquid to the superhydrophobic porous substrate formed a slippery liquid-infused porous surface. A hydrophilic polymer was deposited on top of the superhydrophobic polymer to demonstrate the facile stacking of polymer layers with different chemistries using this process.

5:20pm SS+AS+BI+MI+NS-ThA-10 Atomic-Scale Understanding of Anatase Nanocatalyst Activation, William DeBenedetti¹, E Skibinski, M Hines, Cornell University

Our ability to predict the chemical reactivity of nanocatalysts has been stymied by our lack of atomic-scale understanding of nanocatalyst surface structure. Specifically, do nanocatalyst surfaces adopt a bulk-terminated structure or do they reconstruct to minimize their surface free energy, thereby lowering their chemical reactivity as observed in ultra-high vacuum? Furthermore, do nanocatalysts processed at higher temperature maintain their low-chemical-reactivity, reconstructed surfaces when used at low temperatures and under typical operating conditions?

Using a new technique for the growth of highly aligned anatase (001) nanocatalysts, we will show that solution-synthesized anatase is terminated by a monolayer of fluorine, which acts as an atomic-scale protective coating against adventitious contamination. We will also show that carboxylic acid solutions, the most common TiO_2 functionalization chemistry, causes a spontaneous reorganization of a reconstructed nanocatalyst, leading to a five-fold increase in the number of reactive sites. This surface reorganization is not observed when carboxylic acids are dosed from the gas phase, indicating that experiments in ultra-high vacuum environments lead to trapped states that may not be relevant to nanocatalysts in ambient conditions. *Ab initio* calculations show that although the carboxylic acid termination is slightly less effective at removing surface stress than the reconstructed surface, it is more effective in lowering the surface free energy. These findings suggest that bulk-terminated metal oxide nanocatalysts may be common under ambient operating environments, even after high-temperature processing or if reactants are rinsed off.

5:40pm SS+AS+BI+MI+NS-ThA-11 Mechanistic view of Solid-Electrolyte Interphase Layer Evolution at Li-metal Anode, Venkateshkumar Prabhakaran, Physical Sciences Division, Pacific Northwest National Laboratory; M Engelhard, A Martinez, Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory; G Johnson, Physical Sciences Division, Pacific Northwest National Laboratory; S Thevuthasan, Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory; V Murugesan, Physical Sciences Division, Pacific Northwest National Laboratory

A molecular-level understanding of structural and chemical transformations of electrolyte at solid-electrolyte interfaces (SEI) is critical for rational design of electrochemical materials. Despite numerous studies,

¹ National Student Award Finalist

evolution of the transient and metastable species which dictates the cascade of interfacial reactions are still not clear. The challenge is to establish the chemical homogeneity within interface to clearly delineate the origin of various decomposition reaction products and their energetic pathways. Soft landing of mass-selected ions is ideally suited for building the interface with selected constituent which can alleviate the complexity associated with diverse and correlated processes within SEI layer.¹⁻⁴ Herein, we report the development and first demonstration of new capabilities that combine ion soft landing with *operando* infrared reflection-absorption spectroscopy (IRRAS) to study the decomposition of counter anions and solvent molecules on bare lithium metal surfaces. Specifically, we discreetly deposited sulfonyl imide based electrolyte anion (TFSI⁻) and solvated Lithium cations without corresponding counter ions onto bare lithium metal using soft landing approach and monitored their decomposition using *in-situ* IRRAS and *ex-situ* x-ray photoelectron spectroscopy (XPS). *Operando* IRRAS and XPS measurements captured the signatures of transient species arising from decomposition of electrolyte anions and solvent molecules in real time. We will discuss, our unique approach of building interface with precise control over the constituents and subsequently detect the spectroscopic signatures of transient species during decomposition processes.

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Thursday Evening Poster Sessions, October 25, 2018

Magnetic Interfaces and Nanostructures Division

Room Hall B - Session MI-ThP

Magnetic Interfaces and Nanostructures Division Poster Session

MI-ThP-1 Synthesis and Size Dependent Magnetic Properties of Iron Oxide Nanoparticles, *Jeremy Winsett, A Moilanen, S Neupane*, Middle Tennessee State University

Fe₂O₃, and Fe₃O₄ nanoparticles were synthesized by means of a simple hydrothermal procedure. The experimental parameters were varied to produce nanoparticles of different sizes and morphologies. Variation in growth temperature, duration, precursor concentration, and surfactants will influence the geometry and hence the magnetic properties of nanoparticles. Scanning electron microscopy, transmission emission microscopy and X-ray diffraction were used to characterize as-synthesized magnetic nanoparticles. Saturation magnetization and hysteresis measurement were determined using a vibrating sample magnetometer. Nanoparticles exhibiting size-dependent magnetic properties can find applications in targeted drug delivery, magnetic separation, contrast enhancement in magnetic imaging and others.

Actinides and Rare Earths Focus Topic Room 202C - Session AC+MI+SA-FrM

Actinide and Rare Earth Theory and Related Measurements

Moderators: Paul S. Bagus, University of North Texas, David Shuh, Lawrence Berkeley National Laboratory

8:20am **AC+MI+SA-FrM-1 Periodic Boundary Condition and Embedded Cluster DFT Calculations of Water Adsorption on AnO_2 ($\text{An} = \text{U}, \text{Pu}$) Surfaces, *Nikolas Kaltsoyannis*, University of Manchester, UK, United Kingdom of Great Britain and Northern Ireland **INVITED****

Over half of the World's stockpile of civil plutonium (c. 126 tonnes) is stored at Sellafield in the UK as PuO_2 powder in sealed steel cans. There is evidence of gas generation in some of these cans. Many routes to gas production have been suggested, several of which involve complex, interconnected and poorly understood $\text{PuO}_2/\text{H}_2\text{O}$ interactions.

We have an ongoing project to study computationally the interaction of AnO_2 ($\text{An} = \text{U}, \text{Pu}$) surfaces with water. Standard periodic boundary condition (PBC) implementations of DFT using generalized gradient approximation (GGA) functionals can fail to reproduce key features of actinide solids, e.g. predicting metallic properties in systems known to be insulating. This failure stems from incorrect description of the strongly correlated 5f electrons, which are overly delocalized by the GGA, and the standard solution to this problem is to correct the GGA functionals with an onsite Coulomb repulsion term known as the Hubbard U . An alternative solution is to employ hybrid DFT, in which some of the exact exchange energy of Hartree-Fock theory is incorporated into the Hamiltonian. Such functionals typically produce more localized 5f electrons, and recover insulator behavior. They are, however, extremely expensive to employ in PBC calculations, and hence are rarely used. We have therefore sought a model which allows the routine use of hybrid DFT in AnO_2 /water systems, and have adopted the periodic electrostatic embedded cluster method (PEECM), in which a quantum mechanically treated cluster is embedded in an infinite array of point charges. We treat a cluster of AnO_2 and adsorbing water molecules using hybrid DFT (PBE0) whilst the long-range electrostatic interactions with the bulk are modelled *via* embedding in point charges.

In this presentation, I shall describe the results of both PBC and PEECM studies of the interactions of water with both stoichiometric and reduced (oxygen vacancy) {111}, {110} and {100} surfaces of UO_2 and PuO_2 . The geometries and energetics of single and multiple layers of water will be presented, together with our calculations of water desorption temperatures, from which we propose an alternative interpretation of experimental data.

[1] J.P.W. Wellington, A. Kerridge, J.P. Austin and N. Kaltsoyannis *J. Nuc. Mat.* **482** (2016) 124

[2] B.E. Tegner, M. Molinari, A. Kerridge, S.C. Parker and N. Kaltsoyannis *J. Phys. Chem. C* **121** (2017) 1675

9:00am **AC+MI+SA-FrM-3 Understanding the Role of Oxidation States on the Chemistry of Actinides through Integration of Theory and Experiment, *Wibe de Jong, J Gibson***, Lawrence Berkeley National Laboratory; *R Abergel*, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

Fundamental insights into the role of 5f electrons in the redox chemistry of actinides is essential for predicting the fate and controlling the behaviour of nuclear materials in the ecosystem, as well as for developing new advanced applications in energy, medicine and forensics. In recent years computational chemistry has become a key pillar of multidisciplinary actinide research, advancing the fundamental understanding of actinide chemistry through strong synergies between experiment and simulations. We will present some recent multidisciplinary gas-phase thermochemistry and spectroscopy efforts focused on understanding the role of metal-ligand interactions on the oxidation states of actinides across the series.

9:40am **AC+MI+SA-FrM-5 An Experimentalist's Viewpoint: The Tremendous Strengths and Occasional Weaknesses of Actinide Cluster Calculations, *James G. Tobin***, University of Wisconsin-Oshkosh

Over the course of the last several years, cluster calculations have been used in a myriad of ways to analyze spectroscopic results from actinide systems and gain insight into the electronic structure of these actinide systems. For example, the calculated 6d Unoccupied Density of States (UDOS) in Uranium Tetrafluoride and Uranium Diode were probed using U

L3 (2p) X-ray Absorption Near Edge Structure (XANES) as well as U N7 (4d) X-ray Absorption Spectroscopy (XAS). [1-3] Cluster calculations have also been used successfully to study the development from atomic to bulk electronic structure in Pu [4,5] and issues associated with the 2p Occupied Density of States (ODOS) in Uranium Tetrafluoride. [6, 7] However, there now appear to be some interesting discrepancies between what has been observed experimentally and the predictions of cluster theory. In particular, the F 1s XAS of Uranium Tetrafluoride [8] and the U 4d XAS branching ratio (BR) predictions for oxidized uranium. [1] These issues will be addressed in the talk.

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10:00am **AC+MI+SA-FrM-6 Ligand and Metal XAS Edges in Heavy Metal Compounds, *Paul S. Bagus***, University of North Texas; *C Nelin*, Consultant

In previous work, [1] it has been shown that the magnitude and character of the covalent mixing in representative lanthanide and actinide oxides depends strongly on the nominal oxidation state of the oxide. In the present work, ab initio theoretical wavefunctions, WF, have been determined and have been used to obtain the energies and dipole intensities for different Near Edge X-Ray Absorption (XAS) Fine Structure, NEXAFS edges. The theoretical NEXAFS spectra have been examined in order to determine the extent to which the features of these edges can be used to infer the character and extent of the covalent bonding. An important and novel feature of the theory is that the angular momentum coupling of the open shell electrons is taken into account and the multiplets, both resolved and unresolved, associated with the various NEXAFS features are identified. Furthermore, different sets of variationally optimized orbitals are used for the initial, ground state, and the final, excited state, configurations. Thus, the relaxation and screening in response to the core-hole are taken into account. The systems examined are Ce(III) and Ce(IV) in CeO_2 and U(IV), U(V), and U(VI) in UO_2 . For these systems, cation p and d edges are used to distinguish excitations to the frontier nf and (n+1)d orbitals, especially since it has been shown that both of these cation orbitals have significant covalent mixing with the ligands. The O K-edge NEXAFS is presented and the relative excitation energies and intensities into the cation nf and (n+1)d orbitals are compared to the covalent character of the different systems. The WFs are solutions of the Dirac-Coulomb Hamiltonian. [2] Comparisons are made with experiment to demonstrate the accuracy of the theoretical treatments used.

Support for this work by the Geosciences Research Program, Office of Basic Energy Sciences, U.S. DOE, is acknowledged.

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10:20am **AC+MI+SA-FrM-7 Thermal Expansion and Conductivity of Th and Ac from First Principles Calculations, *Dominik Legut, L Kyvala***, VSB-Technical University of Ostrava, Czech Republic; *U Wdowik*, Pedagogical University, Poland

We investigate electronic structure, lattice dynamics, and thermophysical properties of elemental thorium and made a prediction for actinium as

here the experimental data are scarce. The results were obtained within density function calculations. Recently, Actinium (Ac) shows excellent potential in radiotherapy and Thorium (Th) appears to be a suitable substitution for uranium in novel nuclear fuels. Therefore, we determined the effect of spin-orbit interaction (SOI) for the electronic, elastic, phonon and thermodynamic properties of number of Ac phases (hcp, bcc, fcc, and sc). Similarly, in the case of Th in addition to SOI we investigated also localized versus itinerant behavior of the f electrons. Therefore we applied so-called Hubbard parameter U in the range of 0.5-2 eV for the Th 5f electrons. Next, we calculated the elastic tensor by the linear-response method as implemented in VASP code [1] to determine elastic constants (Cij). Subsequently, the criteria of stability based on Cij were evaluated. Next, we calculated vibrational properties using the direct force-constant method as implemented in the PHONOPY code [2]. Actinium phase transition is discussed within the quasi-harmonic approximation under temperature and pressure to draw different conclusion than in Ref. [3]. We advance our knowledge to predict the thermal conductivity Using the Boltzman transport code [4] we address contribution to the thermal conductivity not only from phonons but also from free electrons. Our determined mechanical and thermodynamical properties of Th show very good agreement with experimental data and give us a high confidence to be able to predict similar properties of Ac and to explain the highest know thermal conductivity of Th among actinides.

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10:40am **AC+MI+SA-FrM-8 XANES Investigation into the Electronic Structure of Ce Coordination Complexes**, *Liane Moreau, C Booth*, Lawrence Berkeley National Laboratory; *Y Qiao, E Schelter*, University of Pennsylvania

Cerium is of particular interest among the lanthanide elements for its stability in both the Ce(III) and Ce(IV) oxidation states. This provides unique redox properties, making Ce a promising candidate for advanced energy materials. To this end, chemistries to control the Ce oxidation state have been widely developed. More interestingly, Ce-ligand bonding has in some cases shown intermediate behavior between Ce(III) and Ce(IV), which is indicative of a multiconfigurational ground state. This phenomenon results in low-energy ligand-to-metal charge transfer in addition to its magnetic behavior, such as temperature independent paramagnetism. In order to understand the effects of Ce electronic structure on compound chemical and physical properties, it is imperative to develop methods to accurately probe the fractional occupancy between $4f^1$ and $4f^0$ configurations.

Ce L₃ edge X-ray absorption near edge structure (XANES) measurements provide detailed information concerning the density of states from varying Ce-ligand bonding configurations. In particular, XANES spectra of Ce(IV) imido, Ce(III/IV) guanidinate-amide and Ce(IV) anilide complexes are presented and related to their specific coordination chemistry. From XANES, lanthanide-ligand bonding covalency is explored. We also consider the effects of varying the alkali metal species in metal-capped Ce(IV) imido. Results from the Ce(IV) complexes exhibit characteristic double white line absorption, indicative of significant 4f orbital participation in metal-ligand bonding. The extent to which covalency is observed is highly dependent on the specific ligand chemistry. In combination with DFT and magnetism results, XANES is used to study the effects of such chemistries on the orbital configurations and relate them to the observed novel properties of Ce coordination complexes.

11:00am **AC+MI+SA-FrM-9 Structure and Properties of Reactively Deposited Uranium Hydride Coatings Studied by the X-ray Scattering Methods**, *Milan Dopita, L Havela, L Horák, E Chitrova*, Charles University, Prague, Czech Republic; *D Legut*, VSB-Technical University of Ostrava, Czech Republic; *M Cieslar*, Charles University, Prague, Czech Republic; *Z Matěj*, MAX-IV, Lund, Sweden

A series of Uranium hydride coatings was prepared using a reactive sputtering method. The samples were sputtered with different Mo doping levels as well as at different hydrogen pressure and various substrate temperature. Fused silica and Si single-crystals were used as substrates for deposited coatings. The structure and the real structure (i.e. the deviations of the structure from the ideal 3D crystal periodicity) of the samples were investigated using the x-ray scattering methods. The x-ray reflectivity yielded the information on the coatings thickness, roughness and electron density. The key results of our work were the determination of the phase composition and its evolution, the description of the coherently diffracting domains - crystallite size and defects distributions, the description of the residual stress, strains and preferred orientation of crystallites - textures and its depth profiles in the coatings.

The sample sputtered on the fused silica substrates crystallized in the β -UH₃ structure (stable uranium hydride phase) with the stress free lattice parameter $a = 0.6703 \pm 0.0004$ nm. The coating exhibited strong 001 preferred orientation of crystallites and compressive residual stress $\sigma = -5.1 \pm 0.1$ GPa. Additionally, the coating revealed a bimodal distribution of crystallite sizes with two components having the mean crystallite size $D_1 = 200$ nm and $D_2 = 3.6$ nm with volume fractions of 60:40, respectively, and huge microstrain in both components. Contrary, the coating sputtered on cooled Si single-crystal substrate showed totally different behavior. It did not form nor the stable β -UH₃ neither the meta-stable α -UH₃ structure. The measured diffraction pattern revealed the fluorite fcc structure, analogous to e.g. PuH₂. This is highly interesting result, since to our best knowledge such form of uranium hydride has not been so far reported in the literature. The polycrystalline coating exhibited tilted *hhh* texture, stress free lattice parameter $a = 0.53598 \pm 0.00014$ nm, compressive residual stress $\sigma = -1.54 \pm 0.09$ GPa and mean crystallite size of 82 nm. Besides, the coating contains pronounced microstrain caused by the crystal lattice defects and significant fraction of the stacking faults. The results of the x-ray scattering studies were correlated with data obtained from HRTEM. Additionally, the possibility of formation of uranium hydride with fcc fluorite structure was confirmed by the ab-initio theoretical calculations (LDA+U).

This work was supported by the project "Nanomaterials centre for advanced applications", Project No. CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF.

11:20am **AC+MI+SA-FrM-10 Ligand Induced Shape Transformation of Thorium Dioxide Nanocrystals**, *Gaoxue Wang, E Batista, P Yang*, Los Alamos National Laboratory

Nanocrystals (NCs) with size and shape dependent properties are a thriving research field. Remarkable progress has been made in the controlled synthesis of NCs of stable elements in the past two decades; however, the knowledge of the NCs of actinide compounds has been considerably limited due the difficulties in handling them both experimentally and theoretically. Actinide compounds, especially actinide oxides, play a critical role in many stages of the nuclear fuel cycle. Recently, a non-aqueous surfactant assisted approach has been developed for the synthesis of actinide oxide NCs with different morphologies, but an understanding of its control factors is still missing to date. Herein we present a comprehensive study on the low index surfaces of thorium dioxide (ThO₂) and their interactions with relevant surfactant ligands using density functional calculations. A systematic picture on the thermodynamic stability of ThO₂ NCs of different sizes and shapes is obtained employing empirical models based on the calculated surface energies. It is found that bare ThO₂ NCs prefer the octahedral shape terminated by (111) surfaces. Oleic acid displays selective adsorption on the (110) surface, leading to the shape transformation from octahedrons to nanorods. Other ligands such as acetylacetone, oleylamine, and trioctylphosphine oxide do not modify the equilibrium shape of ThO₂ NCs. This work provides atomic level insights into the anisotropic growth of ThO₂ NCs that was recently observed in experiments, and thus may contribute to the controlled synthesis of actinide oxide NCs with well-defined size and shape for future applications.

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11:40am **AC+MI+SA-FrM-11 Perspectives on the Synthesis, Characterization and Applications of Upconversion and Downconversion Nanomaterials, Martin Ntwaeaborwa**, University of the Witwatersrand, South Africa

Luminescent nanomaterials incorporating one or more active ions (usually lanthanides) have many uses today in applications such as information displays, light emitting diodes, theft prevention, advertising, medical imaging, photodynamic therapy and photovoltaic cells. In the past few decades, there has been an upsurge of research interest in the synthesis of luminescence down-conversion and up-conversion nanomaterials with different particle morphologies, and their characterization using different optical techniques. The use of lanthanide ions to convert photons either by down-conversion or up-conversion process to different and more useful wavelengths is an interesting research phenomenon for a wide range of applications. For example, the use of down-conversion and up-conversion nanomaterials to improve the power conversion efficiency of crystalline silicon solar cells and for treatment of tumour cells, respectively, have been demonstrated. While efficient down-conversion has been demonstrated from a combination of many rare-earths ions, the most efficient up-conversion has been demonstrated from only a few combination of rare-earths ions such as erbium (Er^{3+}) – ytterbium (Yb^{3+}), thulium (Tm^{3+}) – Yb^{3+} , and holmium (Ho^{3+}) – Yb^{3+} incorporated in different host lattices with low phonon energies. Different mechanisms of luminescence down-conversion and up-conversion will be discussed. In addition, a few selected methods used to synthesise luminescence down-conversion and up-conversion nanomaterials will be discussed.

Magnetic Interfaces and Nanostructures Division

Room 203A - Session MI+EM-FrM

Magnetism and Spin-Orbit Coupling at Surfaces, Interfaces and Thin Films

Moderator: Valeria Lauter, Oak Ridge National Laboratory

8:20am **MI+EM-FrM-1 Interfacial Spin-orbitronics: Spin-charge Current Conversion in Topological Insulators and Rashba Interfaces, Juan Carlos Rojas Sánchez**, Institut Jean Lamour, Université de Lorraine, France **INVITED** Materials with large efficiency of spin-charge current interconversion are highly desirable to study new physical phenomena as well as for spintronics applications. Heavy metals or alloys exhibiting large spin-orbit coupling scatter the electrons in opposite directions when they have opposite spin. Thus an injection of charge current yields a transversal spin current in such materials. The charge-spin current conversion phenomenon in those 3D materials is so-called Spin Hall Effect (SHE). We can exploit this effect to manipulate a magnetization in a heavy metal/ferromagnetic structure [1-3]. We have shown such a manipulation in $\text{Si-SiO}_2/\text{W}(3 \text{ nm})/\text{Co}_x\text{Tb}_{1-x}(3.5 \text{ nm})/\text{Al}(3 \text{ nm})$ structures. Interesting, we have found out that the temperature of the devices reach a novel characteristic temperature just before the magnetization switching takes place [3].

On the other hand, new classes of materials such as 3D topological insulator which are trivial insulator in their bulk but hold metallic states in their surfaces are also highly interesting for spintronics. The spin-orbit coupling (SOC) in the 2DEG states at Topological Insulator (TI) or Rashba Interfaces is predicted to be more efficiency than their 3D counterparts for spin-charge current conversion. Indeed, we have found the highest efficiency at room temperature using the topological insulator $\alpha\text{-Sn}$ [4]. The underlying physics of charge-spin current interconversion in such 2D systems is different of the SHE and is called Edelstein Effect (EE) [5-7], also known as inverse spin galvanic effect [8]. I will show results of spin-to-charge conversion by spin pumping experiments and their analysis in term of inverse Edelstein Length [4-7]. Experimental results based on ARPES and spin pumping indicate that direct contact of metallic ferromagnetic layer is detrimental for the surfaces states of topological insulators but we can keep the surfaces states of $\alpha\text{-Sn}$ using Ag spacer. I will use the conversion parameters obtained at room temperature with $\alpha\text{-Sn}$ to demonstrate the very large advantage of the SOC effects in 2D interface states with respect to the Spin Hall Effect (SHE) of 3D metals and the resulting perspective for low power spintronic devices.

[1] M. Miron, P. Gambardella et al. *Nat.* **476**, 189 (2011)

[2] J.-C. Rojas-Sánchez et al. *APL* **108**, 082406 (2016)

[3] T. H. Pham et al. *arXiv* 1711.10790

[4] J.-C. Rojas-Sánchez et al. *PRL* **116**, 096602 (2016). *ArXiv* 1509.02973 (2015)

[5] J.-C. Rojas-Sánchez et al. *Nat. Comm* **4**, 2943 (2013)

[6] E. Lesne, J.-C. Rojas-Sánchez et al. *Nat. Mat.* **15**, 1261 (2016)

[7] S. Oyarzun, J.-C. Rojas-Sánchez et al. *Nat. Comm.* **7**, 13857 (2016)

[8] S. D. Ganichev et al. *Nature* **417**, 153 (2002)

9:00am **MI+EM-FrM-3 Spin-orbit Coupling in Ion-surface Collisions Observed by a Polarized $^4\text{He}^+$ Ion Beam, Taku Suzuki, O Sakai**, National Institute for Materials Science, Japan

Recently, we found spin-orbit coupling (SOC) act as a mechanism of spin dependent low-energy He^+ ion scattering on solid surfaces. It is intuitively interpreted as the effect on the projectile electron spin of the magnetic field induced by the projectile angular motion around the target nucleus during the projectile-target binary collision (Biot-Savart law). Because a polarized He^+ ion beam is useful for studying surface magnetism, it is important to understand the mechanism of the spin dependent He^+ ion scattering. In the present study, we further investigated SOC from both the experimental and theoretical approaches. In the experiment, electron-spin-polarized $^4\text{He}^+$ ion beam was projected onto the target surface, and the intensity of scattered He^+ ions was measured as a function of their kinetic energy (spin-polarized ion scattering spectroscopy). We found that the scattering angle θ dependence of the spin dependent scattering is remarkably different between the targets of the transition metal and the non-transition metal. This is explained from SOC in the collisional intermediate state, in which an electron of the target is virtually transferred to the He^+ ion.

9:20am **MI+EM-FrM-4 Transport and Magnetic Properties of $\text{LaAlO}_3/\text{SrTiO}_3$ Heterostructure during Cooling and Warming, Zengming Zhang, X Wang**, University of Science and Technology of China, China; *M Zhang, A Rahman, R Dai, Z Wang*, University of Science and Technology of China; *Z Ding*, University of Science and Technology of China, China; *L Cheng*, University of Science and Technology of China

The LaAlO_3 thin films were grown on TiO_2 terminated (001) SrTiO_3 substrate using pulsed laser deposition technique. The transport and magnetic properties of $\text{LaAlO}_3/\text{SrTiO}_3$ (LAO/STO) heterostructure were studied during cooling and warming. The conductivity accelerated recoveries are found at around 70K and 160K for larger electrode interval of several mm, and more obvious for thicker LAO films. This indicated that the domain wall scale increases with the interface variation from fully strain state to partial strain state as the layers of LAO increase. During thermal cycling, both magnetoresistance (xx) and magnetization separate around the conductivity accelerated recovery temperature as seen in Fig. (c). The phenomenon is attributed to the mobile and trapping of defects such as single vacancy and divacancy by polarized domain walls due to the measuring current at the critical temperature [1-2].

References:

1. S. Seri *et al*, Interplay between sheet resistance increase and magnetotransport properties in $\text{LaAlO}_3/\text{SrTiO}_3$, *Phys. Rev. B* **86**, 085118 (2012).

2. S. Seri *et al*, Thermally activated recovery of electrical conductivity in $\text{LaAlO}_3/\text{SrTiO}_3$, *Phys. Rev. B* **87**, 125110(2013).

9:40am **MI+EM-FrM-5 Engineering the Magnetic Properties of Complex Oxide Heterostructures, Yayoi Takamura**, University of California at Davis **INVITED**

Complex oxides possess a wide range of intriguing and technologically relevant functional properties including ferromagnetism, ferroelectricity, and superconductivity. Furthermore, the interfaces of complex oxides have been shown to exhibit unexpected functional properties not found in the constituent materials. These functional properties arise due to various structural and chemical changes as well as electronic and/or magnetic interactions occurring over nanometer length scales at interfaces, and they have the potential to be harnessed to enable new, more versatile, and energy efficient devices. In this talk, I will present some of our recent work investigating the interfacial interactions which occur at ferromagnetic/antiferromagnetic (FM/AF) and FM/FM interfaces. While these interfacial interactions have been widely studied in metallic systems, fundamental differences are observed in complex oxides systems. Specifically, I will discuss FM/FM heterostructures consisting of the soft-FM $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) and hard-FM $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ (LSCO) layers which display a unique exchange spring behavior where the chemical and magnetic interfaces no longer coexist. This phenomena is explained due to the formation of an interfacial layer characterized by magnetically active Co^{2+} ions which forms due to a robust charge transfer interaction at the

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LSMO/LSMO interface. In the second half of the talk, I will discuss the development of measurement protocols for angle-dependent soft x-ray absorption spectroscopy measurements which can be used to unambiguously determine the orientation of the AF spin axis in (111)-oriented heterostructures and to probe how it responds to an applied magnetic field due to exchange interactions with the adjacent FM layer. For the LSMO/La_{0.7}Sr_{0.3}FeO₃ (LSFO) system, the LSFO layers possess two populations of AF order: the majority of AF moments cant out-of-the-plane of the film along low-index crystallographic directions, while a minority of AF moments lie within the (111)-plane. The relative orientation of the AF and FM spins differs for each type of AF domain. These results demonstrate how the many competing interactions in complex oxide heterostructures open up new opportunities to tailor their functional properties for future spintronic devices.

10:20am **MI+EM-FrM-7 Location of the Valence Band Maximum in the Band Structure of Anisotropic 1T'-ReSe₂**, *Markus Donath*, *P Eickholt*, *J Noky*, Westfälische Wilhelms-Universität Münster, Germany; *E Schwier*, *K Shimada*, *K Miyamoto*, *T Okuda*, Hiroshima University, Japan; *C Datzler*, *M Drüppel*, *P Krüger*, *M Rohlfing*, Westfälische Wilhelms-Universität Münster, Germany

Transition-metal dichalcogenides (TMDCs) are a focus of current research due to their fascinating optical and electronic properties with possible technical applications. ReSe₂ is an interesting material of the TMDC family, with unique anisotropic properties originating from its distorted 1T structure (1T'). To develop a fundamental understanding of the optical and electric properties, we studied the underlying electronic structure with angle-resolved photoemission (ARPES) as well as band-structure calculations within the density functional theory (DFT)-local density approximation (LDA) and *GdW* approximations [1]. We observe anisotropic valence-band dispersions parallel to the surface. We find that along ΓM_1 , which is the direction perpendicular to the "diamond" chains, the bandwidth of the highest valence band is significantly smaller than in any other direction. Photon-energy-dependent measurements reveal a k_x -dependent band dispersion, reflecting the interlayer coupling. Two valence band maxima are identified within experimental limits of about 50 meV: one at the high-symmetry point Z, and a second one at a non-high-symmetry point in the Brillouin zone. Thus, the position in k space of the global valence band maximum is undecided experimentally. Theoretically, an indirect band gap is predicted on a DFT-LDA level, while quasiparticle corrections lead to a direct band gap at the Z point.

[1] P. Eickholt *et al.*, Phys. Rev. B **97**, 165130 (2018).

10:40am **MI+EM-FrM-8 Controlling Antiferromagnetic Order at the Surface of La doped BiFeO₃**, *Hendrik Ohldag*, SLAC National Accelerator Laboratory; *B Jang*, Korea Advanced Institute of Science and Technology; *J Lee*, *K Kim*, Korea Advanced Institute of Science and Technology, Republic of Korea; *H Jang*, SLAC National Accelerator Laboratory; *K Ko*, Max Planck Institute for Chemical Physics of Solids; *M Jung*, Pohang University of Science and Technology, Republic of Korea; *Y Koo*, Pohang Light Source; *Y Jeong*, Pohang University of Science and Technology, Republic of Korea; *J Lee*, SLAC National Accelerator Laboratory; *C Yang*, Korea Advanced Institute of Science and Technology, Republic of Korea

Emergence of a triple phase point in two dimensional (*e.g.* pressure and temperature) space can offer useful opportunities for the inter-coupling of two seemingly independent order parameters because of phase proximity. To illustrate the significance of this potential capability we employ a generic concept regarding electric control of magnetic order by manipulating chemical pressure: *i.e.* lanthanum substitution into the model antiferromagnetic ferroelectric BiFeO₃. Our results are made possible by the remarkable finding that a multiferroic triple phase point of a single spin disordered phase and two spin ordered phases emerges near room temperature in Bi_{0.9}La_{0.1}FeO₃ ferroelectric thin films. By using spatially resolved x-ray absorption spectroscopy, we provide direct evidence that electric poling of a particular region of the compound near the triple phase point results in an antiferromagnetic phase while adjacent un-poled regions remain magnetically disordered, opening a promising avenue for magnetoelectric applications at room temperature.

11:00am **MI+EM-FrM-9 Control of Magnetism at the Antiperovskite/Perovskite Interface**, *D Shao*, *T Paudel*, *Evgeny Tsybmal*, University of Nebraska-Lincoln

INVITED

Complex oxide materials with the perovskite crystal structure (ABO₃) are known for their interesting macroscopic physical properties involving the interplay between magnetism, ferroelectricity, and conductivity. Much less explored are the *antiperovskite* compounds (AXM₃) where the atomic

positions of cations and anions are inverted creating unique, wide-ranging properties different from perovskites. Due to the structural similarity, interfaces combining perovskite and antiperovskite compounds can be fabricated, forming a new playground for materials design, where the coupling across the interface may lead to new fundamental properties and functional behavior. Here, based on density-functional calculations, we explore the magnetoelectric effect at the (001) interface between antiperovskite GaNMn₃ and perovskite ATiO₃ (A = Sr and Ba). Bulk GaNMn₃ is an antiferromagnet with the magnetic moments of the Mn ions lying in the (111) planes, forming non-collinear F^{5g} spin configurations with a zero net magnetization ground state. We predict that different from the F^{5g} non-collinear magnetism of the bulk GaNMn₃, strong magnetic moment enhancement and reorientation emerge at the GaNMn₃/ATiO₃ (001) interface, resulting in a sizable net magnetization pointing along the [110] direction. Moreover, switching the ferroelectric polarization of BaTiO₃ leads to reversal of the net magnetization of GaNMn₃. This phenomenon occurs due to the effect of ferroelectric polarization on the magnitude of the antiferromagnetic exchange coupling between the nearest Mn atoms at the interface. Reversal of magnetization by electric means is the holy grail of voltage-controlled spintronics, and thus our results pave a new route to achieve this functionality by exploiting antiperovskite/perovskite interfaces.

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