

Monday Morning, October 19, 2015

Accelerating Materials Discovery for Global Competitiveness Focus Topic
Room: 114 - Session MG+BI+MS+NS+TF-MoM

Development of Novel Materials

Moderator: Talat Rahman, University of Central Florida

9:00am **MG+BI+MS+NS+TF-MoM3 Molecular Engineering of Dyes for Dye-Sensitized Solar Cells via Rational Design, Jacqueline Cole, University of Cambridge, UK** **INVITED**

Dye-sensitized solar cells (DSCs) have unique attributes that afford them prospective applications as smart windows - windows in buildings that generate electricity from sunlight. This electricity will be fed into a local grid that will create sustainable buildings for future cities.

Materials discovery of new DSC dyes is one of the remaining bottlenecks to technological progress of smart windows. This talk shows we are attempting to overcome this materials bottleneck via two complementary routes to molecular design: (i) a 'top down' approach that uses large-scale data mining to identify brand new classes of DSC dyes [1]; (ii) a 'bottom up' approach that computationally transforms well-known non-DSC dyes into suitable DSC dyes [2,3].

The 'top down' approach involves large-scale data-mining to search for appropriate dye candidates [1]. Here, structure-property relationships for DSC dyes have been codified in the form of molecular dye design rules, which have been judiciously sequenced in an algorithm to enable large-scale data mining of dye structures with optimal DSC performance. This affords, for the first time, a DSC-specific dye-discovery strategy that predicts new classes of dyes from surveying a representative set of chemical space. A lead material from these predictions is experimentally validated, showing DSC efficiency that is comparable to many well-known organic dyes.

The 'bottom up' approach concerns case studies on families of well-known laser dyes that are transformed into functional DSC dyes using molecular engineering [2,3]. The underlying conceptual idea is to implement certain electronic structure changes in laser dyes, using molecular engineering, to make DSC-active dyes; while maintaining key property attributes of the laser dyes that are equally attractive to DSC applications. This requires a concerted experimental and computational approach; results predict new dye co-sensitizers for DSC applications.

References

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- [3] F. A. Y. N. Schroeder, J. M. Cole, P. G. Waddell, S. McKechnie, "Transforming benzophenoxazine laser dyes into chromophores for dye-sensitized solar cells: a molecular engineering approach", *Advanced Energy Materials* (2015) DOI: 10.1002/aenm.201401728

10:40am **MG+BI+MS+NS+TF-MoM8 Controlled Spontaneous Nanoscale Patterning of Nonstoichiometric Reconstructions for Catalysis and Light Harvesting, J.M. Martinez, D. Saldana-Greco, University of Pennsylvania, W.A. Saidi, University of Pittsburgh, J.S. Lim, Andrew Rappe, University of Pennsylvania** **INVITED**

The ability to manipulate the atomic and electronic structure and stoichiometry of surfaces is of utmost importance in optimizing heterogeneous catalysts. A critical requirement in this endeavor is a deep thermodynamic and kinetic understanding of surface reconstruction behavior, under various thermal and chemical constraints. We explore the reconstruction behaviors of Ti- and Mn-based perovskite type oxides: BaTiO₃, PbTiO₃, and CaMnO₃: the former two exhibit ferroelectricity, while the latter undergoes surface-induced magnetic ordering. Due to the characteristic properties of these oxides, we investigate the effect of their switchable polarization (for ferroelectric oxides) and near surface magnetic ordering (CaMnO₃) in their surface phase evolution, in addition to the effects of temperature and the chemical potentials of their constituent elements. We find that these oxides undergo surface reconstruction transformations that generally result in enrichment of their catalytically active components (Ti and Mn). These reconstructions show rich bonding and structural motifs that affect the active sites' reactivity and accessibility.

Furthermore, these surface transformations, as in BaTiO₃ and PbTiO₃, can be tuned with the help of an electric field. An applied electric field changes the material's polarization, which then alters the surface electronic properties, and thereby also affects their sensitivity towards stoichiometric changes. In addition to the thermodynamic understanding of the surface reconstructions, we introduce the kinetic tunability of the surface reconstruction. We demonstrate this from a particular surface phase coexistence observed in BaTiO₃, namely the *c*(2x2) and *c*(4x4), where the diffusion behavior of the TiO units that compose both surfaces strongly dictate their degree of agglomeration. Finally, based on our interest in CaMnO₃ (001) surfaces, we have started to explore the more complex CaMn₇O₁₂. The electronic properties of this oxide yield interesting physical phenomena including charge ordering, non-collinear magnetism and improper ferroelectricity. We are currently investigating the ground state non-collinear magnetic configuration in this compound and its role on the stability of the charge-ordered state.

11:20am **MG+BI+MS+NS+TF-MoM10 Developing Evolutionary Algorithms for a priori Crystal Structure Prediction and Applications towards Novel Pressure-Stabilized Materials, Eva Zurek, University at Buffalo-SUNY** **INVITED**

One way to accelerate the development of new materials is via *a priori* crystal structure prediction (CSP) of hitherto unknown systems, followed by the computation of their properties and determination of promising synthesis conditions. A number of algorithms designed to solve global optimization problems have recently been applied to CSP with much success, and evolutionary algorithms (EAs) have emerged as one of the most promising methods for systems where little or no experimental data is available. Therefore, we have developed the open-source XtalOpt EA for CSP as an extension to the widely used chemical builder and visualizer, Avogadro. In this talk we present new developments within XtalOpt that allow it to successfully predict the structures of crystals with larger and more complex unit cells. Furthermore, we summarize the application of XtalOpt towards the prediction of hydrogen-rich solids with unique stoichiometries that are computed to be stable at pressures that are attainable within diamond anvil cells. The influence of the structure of the hydrogenic lattice on the electronic structure and the propensity for high temperature superconductivity is discussed.

Monday Afternoon, October 19, 2015

Accelerating Materials Discovery for Global Competitiveness Focus Topic
Room: 114 - Session MG+2D+MI+NS+TF-MoA

Design and Discovery (Bio and Other Interfaces)
Moderator: Sean Jones, National Science Foundation (NSF), Lynnette Madsen, National Science Foundation (NSF)

3:00pm **MG+2D+MI+NS+TF-MoA3 Rational Accelerated Design of Polymer Dielectrics**, *Rampi Ramprasad*, University of Connecticut
INVITED

To date, trial and error strategies guided by intuition have dominated the identification of materials suitable for a specific application. We are entering a data-rich, modeling-driven era where such Edisonian approaches are gradually being replaced by rational strategies which couple predictions from advanced computational screening with targeted experimental synthesis and validation. Consistent with this emerging paradigm, we propose a strategy of hierarchical modeling with successive down-selection stages to accelerate the identification of polymer dielectrics that have the potential to surpass 'standard' materials for a given application. Specifically, quantum mechanics based combinatorial searches of chemical space are used to identify polymer repeat units that could lead to desirable dielectric properties, followed by configurational space searches to determine the 3-dimensional arrangement of polymers (and their properties) built from the desirable repeat units. Successful synthesis and testing of some of the most promising identified polymers and the measured attractive dielectric properties (which are in quantitative agreement with predictions) strongly supports the proposed approach to material selection.

3:40pm **MG+2D+MI+NS+TF-MoA5 Method to Make a Stable Copper-Carbon Alloy**, *Ivan Shchelkanov, D.N. Ruzic, I. Jasiuk*, University of Illinois at Urbana Champaign

Modern industry demands advanced materials with enhanced properties. To expand a range of available materials the covetic alloy is studied. Covetic is a novel alloy invented and patented by Third Millennium Metals, LLC (TMM). This is a new hybrid material made of a carbon and a metal, where the carbon forms a super lattice structure inside a metal. The base metal can be copper, aluminium, lead, tin or other low-melting point metals. In normal conditions the metal does not wet and does not form chemical bond with the carbon. However, the amount of carbon in the covetic alloy exceeds carbon solubility in the metal by several orders of magnitude. Such a composition is achieved by supplying a current to a volume of molten metal while it is being blended with micron size carbon particles. The alloy is prepared in vacuum.

The process of covetic formation is influenced by chemical composition of the base metal, a cast volume temperature change rate, external electric and magnetic fields, compound viscosity, surface and interphase tension coefficient, density, and thermal and electric conductivities of the metal and carbon particles. A part of the process of covetic alloy formation, which involves carbon particles dissolving, can be compared to phenomena occur in dust plasma. This assumption provides a possibility to visualise processes of microparticles spatial distribution and decomposition into single atoms with subsequent formation of a carbon super lattice inside the metal lattice.

The current work focuses on: the electric current influence on the alloy structure formation and carbon atoms distribution inside the metal; copper covetic hardness, conductivity, and tensile strength change as a function of carbon composition; and a phenomenological model for covetic alloy formation.

4:00pm **MG+2D+MI+NS+TF-MoA6 Development of Nanoporous Solid Phase Microextraction (SPME) Fibers by Sputtering**, *Matthew Linford, C.V. Cushman, B. Singh, A. Diwan*, Brigham Young University

Solid phase microextraction (SPME) is a solventless, fast, easy and relatively inexpensive sample preparation technique that integrates sampling, extraction and preconcentration of samples such as food, waste water, air, and biological fluids in one step. However, commercial SPME coatings may be expensive, show relatively short lives, extract limited numbers of compounds, and have relatively low thermal and mechanical stability. The aim of this study is to develop an SPME device that is thinner, robust, long lasting, has higher mechanical strength, greater thermal and solvent stability, and is devoid of the other drawbacks of commercial coatings. We describe a new method for the preparation of nanoporous SPME coatings via the oblique-angle sputtering of silicon and subsequent

functionalization with silanes. The thickness of the sputtered coatings was controlled by varying the sputtering time. To increase the density of -OH groups on the surfaces, the coatings were treated in piranha solution and then reacted with n-octadecyldimethylmonomethoxysilane to render the surfaces hydrophobic. The coatings were robust and were characterized at each step in the process using XPS, water contact angle goniometry, spectroscopic ellipsometry, and scanning electron microscopy. Our sputtered, silanized fiber yielded comparable and/or better extraction efficiencies than a commercial 7 μm PDMS fiber, especially for higher molecular weight species. In the case of a series of primary alcohols, and aldehydes, our fiber outperformed the commercial PDMS fiber by a factor of 2 - 3. In the evaluation of two real world samples: a sea water extract and beer, our fiber showed unique selectivity. Our 1.1 μm fiber yielded comparable signals to 65 μm PDMS-DVB and 85 μm CAR-PDMS commercial fibers for higher molecular weight analytes. For a ~2.2 μm fiber, the performance of our fiber increased substantially.

Thin Film
Room: 111 - Session TF+2D+MG+NS-MoA

ALD, CVD, MLD, and PLD on Special Materials
Moderator: Giovanna Scarel, James Madison University, Mark Davidson, University of Florida

2:20pm **TF+2D+MG+NS-MoA1 Optical Enhancement of Polyethylene Terephthalate Films Modified by Organometallic Vapor Infiltration**, *Halit Akyildiz*, North Carolina State University, *J.G. Simmons*, Redstone Arsenal, *H.O. Everitt*, Duke University, *J.S. Jur*, North Carolina State University

Polyethylene terephthalate is recyclable thermoplastic polymer that has wide application area including packaging, textiles and insulation applications. Due to the ring structures on the backbone of the polymer it shows weak luminescence in the blue spectrum upon UV light absorption by pi electrons. It has previously been shown that vapors of organometallic ALD precursors are able to infiltrate and react with the polymer to form organic inorganic hybrid materials. Infiltration of trimethylaluminum into PET to form polymer-alumina coordination complexes enhanced the photoluminescence and internal quantum efficiency of the material. In this study we present how the polymer morphology (i.e. crystallinity) and the infiltration temperature are able to affect the optical properties of the resulting PET films. Four unique emission bands are observed in pristine PET films; (2) stronger emissions in high crystallinity films attributed to the crystalline regions of the polymer and (2) peaks that show stronger emission in low crystallinity films attributed to the amorphous regions. After the low temperature infiltration (60 °C) emissions attributed to the amorphous regions demonstrate increases intensity, indicating that the infiltration reaction is predominant in the amorphous regions of the polymer. After infiltration at 150 °C, a very high red shift is observed alongside a complete emission spectra changes, suggesting the reactions taking place at high temperatures are different than low temperature processing. This detailed understanding of the photoluminescence behavior of the hybrid films can provide insight for use of these hybrid materials with a bandgap ideal for unique optical applications.

2:40pm **TF+2D+MG+NS-MoA2 Organic and Hybrid Organic-Inorganic Thin Film Deposition by Resonant Infrared, Matrix-Assisted Pulsed Laser Evaporation**, *Adrienne Stiff-Roberts*, Duke University
INVITED

Over the past fifteen years, matrix-assisted pulsed laser evaporation (MAPLE) has been developed to deposit organic thin films[1-6], inorganic nanoparticles, and hybrid organic-inorganic nanocomposites[4, 7-9]. One variation of the MAPLE technique, resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE), reduces the laser energy (e.g., Er:YAG laser ~2.94 μm peak wavelength) in order to minimize polymer degradation. In addition, because the frequency of the IR laser energy is resonant with OH bond vibrational modes in water, a frozen emulsion (comprising a mixture of the guest material dissolved in an organic solvent and water) is used as the target. Therefore, the unique advantage of emulsion-based RIR-MAPLE is that most of the energy from the IR laser is absorbed by water in the frozen emulsion, which evaporates and gently transfers the guest material to the substrate with minimal solvent exposure and degradation.

In the case of hybrid organic-inorganic nanocomposites, inorganic nanoparticles are embedded in a polymer matrix to achieve specific materials properties or functionality; however, nanoparticles that are mixed

with a polymer in solution tend to aggregate due to a polarity difference with polymers[10]. In contrast, RIR-MAPLE is fundamentally different from solution processing and reduces nanoparticle phase segregation by eliminating the need to co-dissolve nanoparticles and polymers into a single common solvent; and by depositing the nanoparticles and polymers in a relatively dry state.

We will demonstrate the capability of RIR-MAPLE to deposit continuous nanoparticle films with the same optical properties as nanoparticles in solution and to minimize nanoparticle phase segregation in hybrid films. We will also demonstrate hybrid organic-inorganic thin films deposited by RIR-MAPLE for application to solar cells. This work is supported in part by ONR.

References

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3:40pm **TF+2D+MG+NS-MoA5 Integrating Ultrathin ALD/ALE Films with 1D and 2D Materials to Enable New Device Structures.** *Virginia Wheeler, N. Nepal*, U.S. Naval Research Laboratory, *A. Nath*, George Mason University, *A.D. Koehler, Z.R. Robinson, J.K. Hite, K.M. Daniels, M.A. Mastro*, U.S. Naval Research Laboratory, *E. Self, P. Pintauro*, Vanderbilt University, *J.D. Caldwell, R.L. Myers-Ward, D.K. Gaskill, C.R. Eddy Jr.*, U.S. Naval Research Laboratory **INVITED**

As device features continue to approach nanoscale dimensions, requisite structures continually grow in complexity often resulting in 3D architectures, nanowires, and/or 2D van der Waals materials. This reduction in size leads to new phenomena, such as quantum confinement effects in electronics or strong localization of light in nanophotonics, which can potentially enable new devices. Realization of novel device structures that exploit these effects requires integration of scalable thin films of various electronic materials onto nanostructures. Atomic layer deposition (ALD) is the preferred method to conformally coat nominally planar as well as complex, high surface area nanostructures with abrupt interfaces, wafer-scale uniformity, and angstrom-scale control of thickness. Additionally, ALD is a low temperature process which allows incorporation with many temperature sensitive nanostructure materials that are not compatible with other deposition techniques. Alternatively, a slightly higher deposition temperature can facilitate atomic layer epitaxy (ALE) of crystalline thin films with all the same beneficial characteristics of ALD. However, the inert nature of 1D and 2D materials often inhibit direct application of ALD/ALE films with desired coverage and uniformity. In this work, we will discuss crucial aspects of ALD/ALE growth, such as surface functionalization and *in situ* nucleation sequences, required to obtain uniform, conformal films on nanostructured substrates.

The essential requirements for integration of ALD/ALE layers with 1D and 2D materials will be evaluated through several case studies including: 1) integration of III-N films on graphene for a hot-electron transistor; 2) coating of carbon fibers for battery and electrode applications; and 3) functional oxide layers on SiC nanopillars to modify their optical response for several potential devices. The substrates in these cases have varying degrees of surface reactivity, so we will address the need for and our current *ex situ* and *in situ* approaches to obtaining sufficient reactivity between the substrate and ALD precursors. Moreover, it was found that ALD parameters (temperature, pulse and purge durations, etc.) impact the effectiveness of uniform, conformal coating of these structures. Other factors, such as sample suspension, are sometime critical to overcoming these limitations while still operating in ALD/ALE windows. Initial devices results will be presented, when appropriate, to demonstrate the feasibility of the integration of ALD thin films in new device structures.

4:20pm **TF+2D+MG+NS-MoA7 Development of the Optical Properties of Silicon Rich Oxide Films Growth by CVD Techniques for Possible Photovoltaic Applications.** *Karim Monfil-Leyva*, Benemérita Universidad Autónoma de Puebla, Mexico, *A.L. Muñoz-Zurita*, Universidad Politécnica Metropolitana de Puebla, Mexico, *E. Ojeda-Durán, A. Benítez, J. Carrillo-López, J.A. Luna-López, R.C. Ambrosio-Lázaro*, Benemérita Universidad Autónoma de Puebla, Mexico

Currently, electronics and semiconductor studies have focused a great effort to overcome the intrinsic disadvantages of bulk-Si to develop optoelectronic devices. In particular, the Silicon Rich Oxide (SRO) has been proposed as a cheap and effective alternative to develop ultraviolet absorbers or silicon-based light emitters. SRO can be deposited by several chemical vapor deposition techniques like Low Pressure Chemical Vapor Deposition (LPCVD) or Hot Filament Chemical Vapor Deposition (HFCVD). Silicon excess in SRO films obtained by LPCVD can be controlled by pressure ratio $R_o = N_2O/SiH_4$. Meanwhile, silicon excess in SRO films obtained by HFCVD can be controlled by changing the hydrogen flow (H_F).

In this work, we report a study of the optical and structural properties of thin SRO films obtained by LPCVD and HFCVD. Silicon excess was changed by the pressure ratio R_o in the range of 15 and 45 (SRO15 to SRO45) and H_F was changed between 25 and 75 sccm. SRO LPCVD films were annealed at 1100 °C. Ellipsometry and step measurements were applied to calculate thickness and the refractive index. Fourier transform infrared (FTIR) measurements were obtained from SRO films to confirm a change on stoichiometry. Absorbance spectra of SRO films showed rocking and bending vibration modes similar to stoichiometric silicon dioxide but an asymmetric stretching mode revealed the non-stoichiometric nature of our semiconductor films. SRO films by LPCVD showed a strong photoluminescence (PL) at room temperature (RT) on two bands, a blue band from 400 to 550 nm or a red band from 575 nm to 875 nm depending on R_o . Blue and red emission bands were related to donor acceptor decays between traps promoted by defects. SRO films by HFCVD also showed a red band from 500 to 1100 nm (depending on the H_F) and this emission was attributed to defects produced by the transport of the precursors. SRO films showed suitable optical properties for possible photovoltaic applications.

5:00pm **TF+2D+MG+NS-MoA9 Radical-Enhanced Atomic Layer Deposition Enabled Multiferroic Composite Synthesis.** *C. Pham, Jeffrey Chang, J.P. Chang*, University of California at Los Angeles

Multiferroic materials, which exhibit controllable magnetic (ferroelectric) behavior via electric (magnetic) field, are of great interest due to their wide spectrum of new device applications such as non-volatile memory devices. Unfortunately, such behavior is extremely rare in natural single-phase systems. Furthermore, the properties of the few single phase multiferroic materials are too insignificant to be integrated into current device designs. Therefore, alternative strategies involving composite materials are proposed to combine the ferroelectricity and magnetism of different materials, achieving multiferroic behavior. By utilizing piezoelectric and magnetostrictive effects in different material phases, a strain-mediated approach shows great promise for applications. In such a strategy, the interface area per volume, as well as the material crystallinity of each constituent, will greatly influence composite properties. The conformal and high quality film growth with atomic layer deposition (ALD) shows great potential for enabling the multiferroic composites described above.

In this work, lead-free ferroelectric/antiferromagnetic BiFeO₃ (BFO) and ferrimagnetic CoFe₂O₄ (CFO) thin films were grown on SrTiO₃ (001) (STO) substrate by radical enhanced ALD (REALD) using metalorganic precursors, Bi(tmhd)₃ (tmhd = 2,2,6,6-tetramethylheptane-3,5 dione), Co(tmhd)₂, and Fe(tmhd)₃. The use of oxygen radicals as an ALD oxidant provides extra process flexibility. Film crystallinities and properties were studied under different conditions. The BFO films showed epitaxial single crystalline growth in a (001) pseudocubic orientation after annealed at 650 °C while the CFO films are polycrystalline due to the lattice mismatch between the film and substrate (~ 1% for BFO and ~7% for CFO). The piezoelectric properties of BFO films were confirmed using PFM while weak ferromagnetic behavior was also observed. Tunable CFO magnetic properties were shown using thickness-related strain relaxation over the range of 5~90 nm.

Synthesis of multiferroic composites was enabled by REALD. When fixing the total thickness at 40nm, 2-2 BFO/CFO nanolaminate composites with an increasing number of sub-layers showed a controllable competition between magnetic and shape anisotropy. 0-3 CFO/PZT composites were enabled by growing conformal CFO ALD films onto mesoporous PZT medium. SEM confirmed the gradual and conformal coating with increasing ALD cycles. It was found that the pore necks limit the incorporation of CFO inside the mesoporous media as it blocks precursor penetration. The volumetric magnetic properties were found to exceed the values found in literature with 0-3 configurations.

5:20pm **TF+2D+MG+NS-MoA10 Plasma Enhanced Deposition of Nanocrystalline Silicon Thin Films from SiF₄ by RF-PECVD and MDECR: Key Aspects of Growth Dynamics**, *JK. Wang, P. Bulkin, I. Florea, J.L. Maurice, Erik Johnson*, LPICM-CNRS, Ecole Polytechnique, France

For the growth of thin-film hydrogenated silicon by low temperature plasma-enhanced chemical vapor deposition (PECVD), SiF₄ has recently attracted interest as a precursor for numerous reasons, most importantly due to the resilient optoelectronic performance of the resulting layers and devices, even when grown in a slightly oxygen-contaminated growth environment. Nevertheless, many questions remain concerning the critical factors determining the quality of hydrogenated microcrystalline silicon ($\mu\text{-Si:H}$) thin films grown from this precursor.

To advance knowledge on this subject, we present studies performed on two very different types of PECVD reactor: a standard capacitively coupled RF-PECVD reactor, using a process gas mixture consisting of Ar/SiF₄/H₂ and at deposition rates up to 4A/s, and a matrix-distributed electron cyclotron resonance (MDECR) PECVD reactor operating at much lower pressures but achieving a higher deposition rate (8 A/s) and using simply an SiF₄/H₂ mixture. In doing so, we reveal key details concerning the growth process. We underline recently obtained results concerning three critical experimental findings about the use of SiF₄ as a growth precursor: (1) the importance of temperature for high-deposition rate, low-pressure conditions, (2) the vital role of ion bombardment energy on the quality of growth, and (3) the vastly increased challenge of the nucleation process when using high-density plasma processes. The films generated in these studies have furthermore been studied by cross sectional HR-TEM, revealing more specific details about the changing nature of the films during growth, and the dependence of these dynamics on the maximum ion energy impinging on the surface. These studies - along with residual gas analysis studies and optical emission spectroscopy results - allow us to examine the precise growth mechanism of such films when using an SiF₄/H₂ mixture.

Tuesday Morning, October 20, 2015

MEMS and NEMS

Room: 211A - Session MN+MG-TuM

Multiscale Phenomena & Interactions in Micro- and Nano-Systems (8:00-10:00 am) & Optical MEMS/NEMS, Photonics, and Quantum Nanosystems (11:00 am-12:20 pm)

Moderator: Robert Davis, Brigham Young University, Robert Ilic, National Institute of Standards and Technology (NIST), Meredith Metzler, University of Pennsylvania

8:00am MN+MG-TuM1 Microengineering for Mechanobiology, *Beth L. Pruitt*, Stanford University **INVITED**

Living organisms generate and respond to mechanical forces and these forces are sensed and created by specialized cells in the body. Force generation and sensing, or more broadly the mechanobiology coupling tissue (cell) mechanics and biology, are essential in normal development, wound healing, and tissue homeostasis. Our mechanical senses of hearing and touch allow us to navigate our environment and interact with one another, yet they remain the least understood of our perceptive senses. Basic life sustaining functions such as breathing, circulation, and digestion are driven autonomously by coordinated contraction of specialized muscle cells, yet how these functions incorporate active feedback via force sensing at the cellular level is an area of active study. Meanwhile, a variety of specialized stretch activated receptors and mechanically mediated biochemical signaling pathways have been identified in recent years. Importantly, defects in proteins of these mechanically mediated pathways and receptors have been implicated in disease states spanning cardiovascular disease, cancer growth and metastasis, neuropathy, and deafness. Thus, understanding the mechanical basis of homeostasis (health) and defective cell renewal function (disease) increasingly requires us to consider the role of mechanics. To study how cells and tissues integrate mechanical signals, we and others have developed specialized cell cultures systems and micromachined tools to stimulate and measure forces and displacements at the scale of proteins and cells. A key feature of such experiments is the ability to observe cell outputs such as morphological changes, protein expression, electrophysiological signaling, force generation and transcriptional activity in response to mechanical stimuli.

8:40am MN+MG-TuM3 Introducing Students to MEMS: A Practical Process for the Fabrication and Testing of Piezoresistive Cantilevers, *Frederic Loizeau, E. Sadeghipour, T. Larsen, J.Y. Sim, C. Roozeboom, E. Mazzochette, B.L. Pruitt*, Stanford University

We present a laboratory course to introduce students to Micro-Electro-Mechanical Systems (MEMS) through fabrication and characterization of piezoresistive cantilevers. We developed a process flow comprised of only three photolithography steps to minimize time spent by the students in the cleanroom and workload of the teaching team. Students performed hands-on work on over 80% of the fabrication process and thus earned qualification status to operate the standard tools in our cleanroom. The course included practical experience with signal conditioning, noise, and sensitivity measurements. The lab component spanned six sessions of 4.5 hours each and is ideal for integration in a lecture course or a two-week stand-alone mini-course.

The hands-on laboratory component was paired with lectures covering cleanliness, process selection, and device design and characterization. Six lab sessions of 4.5 hours each covered the fabrication and characterization of piezoresistive cantilevers. In each session, teams of five students learned fundamental MEMS processes and equipment use while fabricating pre-designed devices. Weekly homework reinforced design, process, and testing concepts, e.g., predicting device performance, completing lithography steps, or building a measurement circuit. Device fabrication was completed in the first four lab sessions. Modest process support was provided outside of class by the teaching team for batch processes such as wafer preparation, metallization, and final HF release. The yield of the fabrication process was >90%. Each team built their own Wheatstone bridge and amplifier circuit to readout the piezoresistor signal prior to lab sessions 5 and 6 for device characterization. In session 5 they learned to use a dynamic signal analyzer to measure the Hooge and Johnson noise. In session 6, the students measured the power spectral density of cantilever tip deflection due to thermomechanical noise using a laser-Doppler vibrometer (LDV). From these measurements, they estimated the spring constants, resonant frequencies and quality factors of the cantilevers. Using a piezoelectric shaker and the LDV, students simultaneously measured the cantilever

deflection and the piezoresistor bridge output and then used this to calculate cantilever sensitivity and resolution. Finally, experimental measurements were compared with theoretical predictions.

9:00am MN+MG-TuM4 Deflection Control of an Electroactive Polymer Bimorph Actuator by Carrier Frequency Modulation, *Leeya Engel*, Tel Aviv University, Israel, *K. Van Volkinburg*, University of California Irvine, *Y. Shacham-Diamand*, Tel Aviv University, Israel, *G.N. Washington*, University of California Irvine, *S. Krylov*, Tel Aviv University, Israel

In microelectromechanical systems (MEMS), actuator deflections are typically controlled by varying the voltage used to drive the active element. In this work, we use the frequency sensitivity of the permittivity of relaxor ferroelectric polymer poly(vinylidene fluoride-trifluoroethylene chlorotrifluoroethylene (P(VDF-TrFE-CTFE))) as an additional parameter for controlling the deflections of an electroactive polymer bimorph actuator.

The amplitude of the tip deflection of the electroactive polymer bimorph actuator, whose active layer comprised a thin film of P(VDF-TrFE-CFE), increased with the voltage applied at constant frequency, as expected. When the peak-to-peak displacements of the beam were plotted as a function of frequency at constant peak-to-peak voltage, a nonlinear decrease in tip deflection with increasing frequency was observed, independent of the resonance of the device. Electrical characterization of the material shows that the real component of the permittivity is ~ 55.5 at 100 Hz, but at radio frequencies, it decreases to 4. Dielectric losses are high at frequencies on the order of kHz–GHz with a coefficient of loss above 60% around MHz frequencies. Thus, the decrease in magnitude of electromechanical displacement with frequency can be attributed to the decrease in the permittivity-dependent electric field related electrostrictive coefficient with frequency. Deflections were recorded using both a laser Doppler vibrometer (LDV) and by interpreting the potential difference that formed across an integrated layer of piezoelectric polymer PVDF during actuation. In addition to adding mechanical sensing capabilities to the device, the PVDF layer also functioned as the passive layer of the bimorph structure.

This work directly demonstrates the dependence of the electromechanical behavior of an electroactive polymer actuator on the dielectric properties of P(VDF-TrFE-CFE) and our ability to exploit that dependence for an additional control parameter of the device. Frequency modulation of polymer beam deflections and integration of sensing capabilities can benefit the developing field of polymer microactuators, in applications such as "smart" prosthetics and implants, targeted drug delivery, tools for less invasive surgery, microfluidics, and on-chip cooling.

9:20am MN+MG-TuM5 Solder Based Self-Assembly Method For 3D Integration Using Poly-Acrylic Acid, *Connor Smith, Y. Feng, S.L. Burkett*, The University of Alabama

The use of Solder Based Self-Assembly (SBSA) in fabricating 3D structures on the microscopic scale is a process with numerous potential applications. This method involves creating copper plated 2D flat patterns of various shapes on a silicon substrate. Then, upon dip soldering these patterns and re-flowing the solder with hydrochloric acid, surface tension pulls up on these shapes to form a 3D structure. However, the use of a SiO₂ sacrificial layer in performing this method results in the need for hydrofluoric acid (HF) during the etching phases, which has many dangerous hazards associated with it. The goal of this research is to develop a new process in which a water-soluble polymer, poly-acrylic acid (PAA), may be used as a sacrificial layer instead of SiO₂--thus making the micro-fabrication process much safer. By working through the original SBSA method, and overcoming the various obstacles created by needing to protect the PAA from being exposed to water earlier than desired, an effective procedure has been developed. Through completing this project, future attempts to fabricate microscopic 3D structures using the SBSA method will be safer and less prone to dangerous HF exposure. Furthermore, removing HF etching from the procedure will reduce the time required to move through the process as a whole, thus increasing its efficiency.

11:00am MN+MG-TuM10 Mechanics and Spins in Diamond, *A. Bleszynski Jayich, Donghun Lee*, University of California at Santa Barbara **INVITED**

Single crystal diamond mechanical resonators have recently emerged as a promising platform for hybrid quantum systems comprising spins and phonons. Diamond mechanical resonators exhibit exceptionally high quality factors¹ and diamond plays host to a highly coherent spin system: the nitrogen vacancy (NV) center. The NV center is an atom-sized defect in diamond that is a remarkably good sensor of magnetic, electric, thermal, and strain fields on the nanoscale. Because of its strain sensitivity, the NV

can be easily coupled to a mechanical degree of freedom. We have recently characterized the sensitivity of the NV's ground state spin to strain by controllably applying dynamical strain to NV centers embedded inside high quality factor diamond mechanical resonators². We have also recently demonstrated strain-mediated coupling to the optical transitions of single NV centers. Through strain coupling, we show that coherent mechanical control of individual spins in diamond is possible. These results are encouraging for proposals to use such a spin-mechanical platform for spin-squeezing, phonon-mediated spin-spin interactions³, and phonon cooling of macroscopic mechanical resonators⁴. We discuss the necessary steps needed to reach these goals and current progress including improvements in diamond fabrication, NV formation, and readout techniques.

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11:40am **MN+MG-TuM12 Nano-Optomechanical Fin Resonators Designed for Sensing in Liquid Environments, Jocelyn Westwood-Bachman, W.K. Hiebert**, University of Alberta and The National Institute for Nanotechnology, Canada

Nanomechanical systems are well known for their mass sensitivity, and are often used as mass sensors [1]. However, nanomechanical sensors tend to operate poorly in liquid environments due to viscous damping by the surrounding fluid. This drawback is particularly challenging for biological and related clinical sensing applications, where it is ideal to detect molecules within a liquid environment [2]. Here, we show the design of a fin-like nanomechanical resonator specifically for use in liquid environments. This design features a cantilever pointing out of the plane of the silicon device layer. This is in contrast to typical cantilevers that are in the silicon plane. The length of the cantilever is determined by the thickness of the silicon layer used, and the thickness of the resonator is designed to achieve specific resonance frequencies. The motion of these fin-like resonators is read out by an adjacent photonic microring resonator [3]. This microring resonator also provides an avenue for optical actuation of the fin resonator. The benefit of this design over existing designs is twofold. Firstly, our integrated photonics detection and actuation scheme provides higher displacement sensitivity than interferometric techniques [4]. Secondly, the fin is designed to operate at high frequencies (above 500 MHz) but can still have comparable surface area to nanoscale cantilevers as the width can be made arbitrarily large. This increases the sensing area while reducing the overall dissipation [5]. We will illustrate our design methodology and show the first generation of devices. As the as-fabricated devices have larger-than-desired feature sizes due to the limitations of photolithography, we will also discuss potential methods of tuning the device size post-fabrication. Specifically, we explore the possibility of trimming the fin resonator using Ga and He ion milling.

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12:00pm **MN+MG-TuM13 Directed Magnetic Optical Resonator Microballoons for Particle Imaging Manometry in 3D Environment, Niladri Banerjee**, University of Utah

Measurement of velocity and pressure field in microfluidic 3D environment is vital in complete characterization of any fluid flow for capillary networks, flow-based separators and microchips for different biological applications. Particle imaging velocimetry though is the gold standard for measuring in-flow velocity, there has been no equivalent technique to perform pressure mapping. Recently hollow spherical micro-particles were fabricated to perform pressure measurement inside microfluidic channels. But lack of control on the trajectory of these particles inside micro-channels resulted in the inability to perform on-the-fly in-flow pressure mapping by spectroscopic method at any arbitrary location.

In this paper, we present the design, fabrication and testing of engineered magnetic micro-balloon pressure sensor particles. These directed particles, when injected into the flow-stream of any microchip, can be localized at

any specific location of interest for dynamic pressure measurement. Each particle consists of a vacuum sealed spherical cavity along with a gold-nickel-gold magnetic tail attached to a polymeric support stem. The hollow cavity sealed by a thin polymeric shell, behaving as a Fabry-Perot interferometer, changes in size due to external pressure variation, which is detected by spectroscopic technique. Moreover the magnetic tail enables temporary immobilization of these particles at any position in the channel by the application of external magnetic field. The fabrication of these particles is based on buried sphere technology (BST). The fabrication starts with patterning of circular holes on thermally oxidized silicon. A trench 10-15 μm deep into the substrate is etched by DRIE. Next we oxidize the sample to grow 100 nm of oxide in order to protect the sidewalls of the trench. On selectively etching oxide from trench-bottom wall, spherical cavity of 6 μm radius is etched by XeF_2 . Then the spherical cavity is smoothed and hole necked down by subsequent oxidation and poly-deposition process steps. Al_2O_3 is then deposited by ALD forming a gas leakage-stop layer followed by parylene-C, to form the micro-balloon wall. Then a gold-nickel-gold (0.2-0.5-0.2 μm) sandwich is sputtered and encapsulated using another 1 μm layer of parylene-C. Real-time in-flow pressure measurement using 0.1T permanent magnet is performed at 8 magnet-specified locations with particles dispersed in IPA inside a serpentine test-chip. Spectral reflectance measurement indicates a pressure sensitivity of 37nm/psi. The paper will discuss the fabrication and test of the magnetic particles in detail with additional internal pressure measurement examples.

Wednesday Afternoon, October 21, 2015

Nanometer-scale Science and Technology

Room: 212B - Session NS+EN+MG+SS+TF-WeA

Nanoscale Catalysis and Surface Chemistry

Moderator: Sidney Cohen, Weizmann Institute of Science, Israel

2:20pm NS+EN+MG+SS+TF-WeA1 Effects of γ -Al₂O₃ Support on the Geometry and Electronic Structure of H-covered Pt Nanoparticles, *Sampyo Hong, G. Shafai, T.S. Rahman*, University of Central Florida

We have studied the effects of γ -Al₂O₃(110) support on the geometry and electronic structures of H-covered Pt_x (x=22,44) nanoparticles (NP) using density functional theory (DFT). We find that the unoccupied d-band center of γ -Al₂O₃(110) supported Pt NPs exhibits a blue shift with decreasing Pt size similarly as the measured XANES absorption peak energy of Pt NP samples. In fact, our DFT results reveal that the shift of the unoccupied d-band center of Pt NPs is dependent of surface hydroxylation level on γ -Al₂O₃(110). At higher hydroxylation the calculated unoccupied d-band center can even show red shift. Thus, consideration of hydroxylation level on γ -Al₂O₃(110) is needed to properly interpret support effect from XANES spectra. Overall, the strength of Pt- γ -Al₂O₃(110) binding seems to be a reasonable measure of the shift of unoccupied d-band center as a result of metal-support interaction: the stronger the interaction the more the blue shift. In the light of these results, it is plausible to postulate that the adsorption energy shift of XANES spectra represent the strength of metal-support interaction (support effect). A remarkable example of such hydroxylation tuned metal-support interaction is structural transition of Pt₂₂ from a biplanar to a 3D-like geometry as a function of support hydroxylation.

This work is supported in part by DOE Grant DE-FG02-07ER15842.

3:00pm NS+EN+MG+SS+TF-WeA3 Fabrication and SERS Activity of Metal-loaded TiO₂ Nanometer Scale Particles, *Paolo Reyes, J.C. Hemminger*, University of California Irvine

Our current research focuses on the fabrication and study of metallic loaded titanium dioxide (TiO₂) nanoparticles supported by highly oriented pyrolytic graphite (HOPG). Highly dispersed TiO₂ particles are formed via physical vapor deposition (PVD) under high vacuum settings with an average pseudo-diameter of 11.6 ± 2.65 nm. Metallic loading is completed by an ex-situ photo-deposition method by exposure to precursor metal salt solutions under TiO₂ bandgap UV irradiation. We have attempted to fabricate Pt-, Ag-, Au-, and Pt-Au-TiO₂ particles and observed photocatalytic enhancement with the inclusion of Pt nanoparticles deposited onto TiO₂ surfaces. We believe this enhancement is a result of Pt nanoparticles harboring free excited electrons and preventing electron-hole recombination. We have developed a technique to increase the density of TiO₂ particles by creating site defects on the surface of HOPG through plasma mild oxygen plasma exposure. Highly dispersed TiO₂ nanoparticle distributions allow an increase of metal nanoparticle formation on TiO₂ for surface and intrinsic property observations. Ag nanoparticles have been fabricated in order to observe Surface Enhanced Raman Spectroscopy (SERS) Ag nanoparticles were observed to be an average pseudo-diameter of 2.6 ± 1.4 nm. A probe molecule was used to determine Raman intensity enhancement factor (EF) and we believe that the EF can be affected by the spacing and size of Ag-TiO₂ nanoparticles. We will present our studies of bi-metallic loading of TiO₂.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences through grant number: DE-FG02-96ER45576

4:20pm NS+EN+MG+SS+TF-WeA7 Pyridine Coordination Chemistry for Molecular Assemblies, *Milko Van der Boom*, Weizmann Institute of Science, Israel **INVITED**

Many types of metal-ligand interactions have creatively been used in the chemical sciences since the description of coordination complexes. The rich coordination chemistry of pyridine-type ligands has contributed significantly to the incorporation of metal ions into functional materials on surfaces. We will discuss molecular assemblies formed with a variety of pyridine-based compounds. These assemblies are formed by layer-by-layer deposition from solution that allows for precise fitting of the assembly properties. The degree of intermolecular interactions can be controlled by varying the degree of π -conjugation and the availability of coordination sites. Unlike molecular assemblies that are constructed with organic ligands, assemblies with polypyridyl complexes are active participants in their own

formation and amplify the growth of the incoming molecular layers. Such a self-propagating behavior for molecular systems is rare and the mechanism of their formation will be presented. Incorporating multiple metal complexes into a single assembly give rise to composite materials that exhibit unique electrochemical and electrochromic properties that are dependent on the arrangement of these metal complexes. We will also discuss the coordination chemistry of pyridine-based compounds with nanoparticles, the formation of metal-organic frameworks and their practical applications.

5:00pm NS+EN+MG+SS+TF-WeA9 Atomic Scale Iron Carbide Films on Au(111) and Cu(111) as a Iron Fischer-Tropsch Model Catalyst, *Gilbère Mannie, X. Wen, Y.W. Li*, SynCat@Beijing, China, *J.V. Lauritsen*, Interdisciplinary Nanoscience Center (iNANO), Denmark, *H.J.W. Niemantsverdriet*, SynCat@Beijing, China

Iron-based Fischer-Tropsch synthesis (FTS) is one of the most investigated catalytic systems in the world due to the ability to convert any form of hydrocarbons like coal, natural gas or biomass into diesel, gasoline and chemicals [1]. Although investigated for more than 50+ years, fundamental surface reactions involved in this process are not known or fully understood. Within the FTS community, iron carbide is seen as the active phase in the catalytic process but the atomic-scale surface structure and even the stoichiometry of the bulk phase is a matter of debate [1,2]. In order to fundamentally investigate the active phase, to for example verify molecular modeling studies on iron carbide surfaces (like [3,4]), we successfully synthesized highly-crystalline iron carbide monolayer islands (on Au(111)) and multilayer islands (on Cu(111)). Obtained carbidic films are suitable for analysis with scanning tunneling microscopy (STM) and other surface science techniques. Our atomically-resolved STM results, together with preliminary density functional theory (DFT) results show that we can characterize our iron carbide (Fe_xC_y) islands as iron layer with interstitial carbon atoms, based on the increase of the inter-atomic Fe-Fe distance [5]. During the synthesis of the Fe_xC_y islands we were able to record some STM movies showing the formation of the carbidic phase out of the metallic phase but we could also record movies during dosing experiments of several gasses (H₂, O₂) to the pure iron carbide islands. During the presentation we will explain how we synthesized these crystalline iron carbide films and how these films can act as a model system for fundamental Fischer-Tropsch catalyst research.

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5:20pm NS+EN+MG+SS+TF-WeA10 Fullerene Interaction with W Surfaces: Synthesis of Nanospheres with Tunable Bandgap, *Ehsan Monazami*, University of Virginia, *J.B. McClimon*, University of Pennsylvania, *P. Reinke*, University of Virginia

The interaction of f C₆₀ molecules with metal surfaces is a topic of considerable interest and discussed in the context of molecular electronics and organic solar cell applications. Our work focuses on the interaction of C₆₀ with W, which is a carbide forming transition metal. It has generally been assumed that the C₆₀ cage breaks up readily on a W surface, but our observations reveal a more complex, temperature induced reaction sequence leading to the formation of nanospheres with variable bandgap, which has been studied with in-situ STM and STS analysis.

The nanospheres are synthesized by initiating the reaction between C₆₀ deposited on a W-thin film surface grown on MgO(001) at about 450 K. In contrast to previous reports, the molecules do not collapse but the spherical shape is retained up to 800 K and the electronic structure changes gradually from wide bandgap C₆₀ to fully metallic nanospheres. The size distribution of the nanospheres is centered at 1.5 nm (600 K) and shifts for higher temperatures to about 2 nm with a concurrent decrease in height resulting in an ellipsoidal shape. These nanospheres present an exceptional resistance to sintering which is a unique feature for metallic nanoparticles. The densely packed C₆₀ and isolated C₆₀ molecules show the same transition in shape and electronic structure which confirms that the transformation is controlled by the reaction with the W substrate.

The transition in the electronic structure progresses gradually from the wide-bandgap molecule (2.3 eV) to a bandgap of ~1eV at 700 K, and a metallic surface at 800 K. We will illustrate this progression with a series of

ST spectra and maps. The bandgap variation offers for the first time a pathway to the formation of nanoscale clusters (nanospheres) with variable bandgap while retaining the surface curvature in narrow range. The detailed structure of the nanospheres is, however, still subject to discussion. We currently favor, based on our experimental results, a substitution model where the W-atoms from the substrate react with the C₆₀ cage which acts as a scaffold. The W atoms are incorporated substitutionally forming a carbide type bonding, whose presence is indicated by XPS analysis. The variation in bandgap is then driven by the degree of substitution and the fullerene molecule acts as a scaffold. We predict that other carbon scaffolds such as nanotubes and carbide forming transition metals can react in the same manner leading to a new class of nanostructures with unique adaptability of the electronic structure. The nanospheres are an excellent testbed for the physics and chemistry of highly curved surfaces.

Supported by NSF-DMR Ceramics DMR-100580.

5:40pm **NS+EN+MG+SS+TF-WeA11 Enantiomeric Separations of Chiral Pharmaceuticals using Chiral Tetrahedral Au Nanoparticles**, *Nisha Shukla, D. Yang, A.J. Gellman*, Carnegie Mellon University

Chiral tetrahedral (24-sided) Au nanoparticles are tested for their use as chiral separators of pharmaceutical drugs in solution phase. Tetrahedral Au nanoparticles were chirally modified with either D- or L-cysteine. They show enantioselective adsorption of pharmaceuticals such as propranolol hydrochloride (used for anxiety and high blood pressure) from a solution of racemic propranolol hydrochloride, thus leaving an enantiomeric excess in the solution phase. This work suggests that chiral nanoparticles can be used for enantiomeric separation of real pharmaceutical drugs. A simple robust model has also been developed that allows extraction of the enantiospecific equilibrium constants for R- and S-propranolol hydrochloride adsorption on the chiral tetrahedral Au nanoparticles. The model obviates the need for experimental determination of the surface area of absorbent Au nanoparticles which is extremely difficult to measure.

6:00pm **NS+EN+MG+SS+TF-WeA12 Electroreduction Catalysis with Defect-Rich Metal Nanoparticles**, *Xiaofeng Feng, M. Kanan*, Stanford University

New design principles for electroreduction catalysts are essential for CO₂ recycling using renewable electricity. Au is one of the most active catalysts for CO₂ reduction to CO, and numerous efforts have been made to optimize Au catalysts by tuning the size, composition, and shape of Au nanostructures. Here we show that grain boundaries (GBs) in Au nanoparticles create highly active surface sites for CO₂ electroreduction (1). Defect-rich Au nanoparticles were synthesized by vapor deposition of Au onto a carbon nanotube thin film, which enables direct TEM characterization without further processing. We compared the CO₂ reduction activity of the as-deposited catalysts to those annealed at different temperatures. While the annealing process has little impact on the distribution of Au surface facets, it reduces the GB density, which is quantified by measuring GB lengths and particle areas from high-resolution TEM images. We found that the surface-area-normalized activity for CO₂ reduction is linearly correlated with GB density in Au nanoparticles in the low overpotential regime. Similarly, GB-density was also found to correlate with catalytic activity for the electroreduction of CO to multi-carbon oxygenates on Cu nanoparticles. Our studies show that grain boundary engineering is a general strategy for improving electrocatalytic activity for carbon fuel synthesis.

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Thursday Morning, October 22, 2015

2D Materials Focus Topic

Room: 212C - Session

2D+EM+MG+NS+SE+SM+SS+TF-ThM

Emergent 2D Materials

Moderator: Paul Sheehan, Naval Research Laboratory

8:00am **2D+EM+MG+NS+SE+SM+SS+TF-ThM1 CVD Growth and Characterization of 2D MoS₂, MoSe₂, MoTe₂, WS₂, WSe₂, and MoS₂(1-x)Se_{2x} Alloys**, David Barroso, T. Empante, A. Nguyen, V. Klee, I. Lu, E. Preciado, C. Lee, C. Huang, W. Coley, S. Naghibi, G. von Son, A. Brooks, J. Kim, L. Bartels, University of California, Riverside

Transition Metal Dichalcogenides (TMDs) have been of increasing interest over the past years due to their exciting semiconducting properties. In the bulk, TMDs possess a native indirect bandgap and transition to a direct bandgap as they approach the monolayer limit. The bandgaps range from 1.15 eV to 1.95 eV depending on composition. Using organic liquids and/or inorganic powders as precursors, CVD growth techniques have been realized for MX₂ TMDs (M = Mo, W; X = S, Se, Te) and their alloys at tunable compositions. We achieved consistent synthesis of these TMDs materials. The films can either be made homogeneous in bandgap or exhibiting a linear bandgap gradient. Characterization of the films include Raman and photoluminescence spectroscopy, as well as AFM. Device fabrication allows for transport measurements. Depending on the composition, the materials show n- or p-doping in a consistent fashion.

8:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM2 Investigation of Manganese Dioxide Nanosheets by STM and AFM**, Lorraine Vernisse, S. Afsari, S.L. Shumlas, A.C. Thenuwara, D.R. Strongin, E. Borguet, Temple University

Interest in ultrathin two-dimensional nanosheets has grown exponentially thanks to their unique and diverse electronic properties. As they possess atomic or molecular thickness and infinite planar dimension, they are expected to have different properties than the bulk of the material from which they originate. This offers opportunities for the development of devices in various areas, ranging from catalysis to electronics. Using the exfoliation approach, it is possible to investigate 2D nanosheets of different materials in search of new phenomena and applications. Bearing this mind, we focused on manganese dioxide (MnO₂), and more specifically δ-MnO₂ (Birnessite). This mineral has the advantage to present a low surface enthalpy [1], which results in weak water binding. Moreover, the presence of defects, e.g., oxygen vacancies has a dopant effect on water oxidation. These properties make MnO₂ a perfect candidate as a catalytic surface for water splitting and pave the way to the design of clean and renewable energy system. Furthermore, MnO₂ can be easily exfoliated into ultrathin nanosheets owing to the layered structure of the manganese oxide precursors.

Our goal is to investigate the catalytic activity of ultrathin MnO₂ nanosheets using scanning probe microscopy techniques, especially atomic force microscopy (tapping mode) and scanning tunneling microscopy (ambient and electrochemical conditions). In this perspective, we have first improved the deposition processes and find the imaging conditions to observe MnO₂ nanosheets with an average thickness of one or two layers. We have also showed that MnO₂ single layer nanosheets exhibit an expected hexagonal atomic pattern and present some defects. We will now resolve and identify the different defects and investigate the evolution of the conductivity as a function of the defect concentration and the number of layers.

This work was supported as part of the Center for the Computational Design of Functional Layered Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0012575.

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8:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM3 Two-Dimensional Early Transition Metal Carbides and Carbonitrides "MXenes": Synthesis, Properties and Applications**, Michael Naguib, Oak Ridge National Laboratory

INVITED

Ternary layered carbides and nitrides with formula of M_{n+1}AX_n (M stands for early transition metal, A for group A element, X is carbon or nitrogen, and n=1, 2, or 3), so called MAX phases, are known for their unique combinations properties of ceramics and metals. It was found recently that etching atomically thin layers of aluminum from the MAX phases results in

forming weakly bonded stacks of two-dimensional (2D) layers of early transition, coined as MXenes. The etching was carried out in fluoride contained aqueous systems. Thus MXenes surfaces are terminated with a mixture of groups including OH, O, and F. Sonicating MXenes in water results in delaminating few layers of MXenes from each other. However, to achieve a large-scale delamination, intercalation of a large compound between the layers prior to delamination is needed. MXenes were found to be a very interesting family of 2D materials since they are electrically conductors and hydrophilic. They also showed an excellent performance as electrodes for electrochemical super capacitors and Li-ion batteries. Here the recent progress in MXenes research from the synthesis to properties and applications will be covered, and in more details, large-scale delamination of MXenes will be discussed. Also, light will be shed on the performance of MXenes as electrode materials for electrochemical energy storage systems.

9:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM5 Molecular Beam Epitaxy of Large area HfSe₂(ZrSe₂)/MoSe₂ van der Waals Heterostructures on AlN(0001)/Si substrates**, Athanasios Dimoulas, P. Tsipas, E. Xenogiannopoulou, D. Tsoutsas, K.E. Aretouli, J. Marquez-Velasco, S.A. Giamini, N. Kelaidis, NCSR DEMOKRITOS, Greece

Two dimensional (2D) semiconductor van der Waals heterostructures (HS) made of group IVB (Zr, Hf) and group VIB (Mo, W) metal dichalcogenides are predicted [1] to have type II or type III band alignments mainly because of a large difference in their workfunctions and band gaps, which makes them candidates for novel 2D staggered, or broken gap tunneling field effect transistors (TFET). We use molecular beam epitaxy (MBE) to grow high quality large area HfSe₂ [2,3], ZrSe₂ [4] and MoSe₂ [5] films directly on AlN(0001)/Si(111) substrates. We confirm by RHEED and HRTEM that atomically thin layers (1-6 ML) are grown in single crystal form with a well-defined in-plane orientation on AlN. The films are continuous with smooth surface morphology (0.6 nm RMS roughness) and abrupt interfaces with no detectable reaction as verified by in-situ XPS and HRTEM. Micro Raman mapping for all layers confirms their structural integrity down to one monolayer and reveals very good uniformity on a cm-scale wafer and excellent stability of MoSe₂ over a period of at least two weeks in air. Strong room temperature PL signal of 1 ML MoSe₂ indicate high quality direct gap semiconductor in agreement with valence band structure details imaged by our in-situ ARPES [3, 5]. In a second step, MoSe₂/HfSe₂ [3] and MoSe₂/ZrSe₂ [4] HS were grown. Despite the large lattice mismatch, all layers are grown epitaxially as evidenced by RHEED with no detectable defects at the interfaces as confirmed by HRTEM suggesting good quality vdW epitaxy [6]. Using UPS the workfunctions (WF) were estimated to be 5.2, 5.5 and 5.4 eV for MoSe₂, HfSe₂ and ZrSe₂ respectively [3,4]. The last two differ substantially from theoretical values (~ 6 eV). Based on our STM and DFT calculations [3], we conclude that this difference is due to an ordered Se adlayer which lowers the HfSe₂ and ZrSe₂ WF bridging the WF gap between them and MoSe₂. As a result, small valence band offsets of 0.13 and 0.58 eV were found for the HfSe₂/MoSe₂ and ZrSe₂/MoSe₂ HS, respectively leading to type II band alignments. The availability of low cost wide-gap-AlN/Si wafers in 300 mm wafer sizes defines a manufacturable route for single crystal 2D semiconductor technology.

We acknowledge financial support from ERC Advanced Grant SMARTGATE-291260. We thank IMEC for providing the AlN/Si substrates.

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9:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM6 Surface Investigation of WSe₂ Atomically Thin Film and Bulk Crystal Surfaces**, Rafik Addou, H. Zhu, University of Texas at Dallas, Y.-C. Lin, S.M. Eichfeld, J.A. Robinson, Penn State University, R.M. Wallace, University of Texas at Dallas

Heterogeneous fabrication of semiconducting two-dimensional layered materials presents a promising opportunity to develop highly tunable electronic and optoelectronic materials. (1-2) An example of crystalline monolayer of WSe₂ grown by chemical vapor deposition on epitaxial graphene (EG) grown from silicon carbide had been investigated at nanoscale level. The WSe₂ surface was characterized using atomic force microscopy (AFM) scanning tunneling microscopy/spectroscopy (STM/STS) and X-ray photoelectron spectroscopy (XPS). (3,4) AFM and

large STM images show high-quality WSe₂ monolayers. The sharpness of the W 4f and Se 3d core levels confirms the absence of any measurable reaction at the interface and oxide formation. The photoemission measurements of WSe₂-Graphene interface suggest p-type doping due to charge transfer (EG withdraws electrons from WSe₂) at the interface and formation of Schottky-type contact,(5) suggesting possible applications of such heterostructures as diodes and photodetectors. High-resolution STM images reveal atomic-size imperfections induced by Se vacancies and impurities. Additionally, the investigation of bulk WSe₂(0001) surface shows spatial variation attributed to the presence of two components in W 4f_{7/2} core level attributed to the presence of both n- and p-type behavior. STM images exhibit also various types of defect induced by vacancies and dopants. The STS spectra reveal two main characteristics i) expected p-type conductivity where the Fermi level located at the valence band edge, and ii) zero conductivity at negative bias explained by defect-induced band bending as reported on geological MoS₂ crystal surfaces.(4) In conclusion, the spatial variation (topography and electronic structure) is more noticeable in bulk WSe₂ grown by chemical vapor transport than in CVD thin films.

This work was supported in part by the Southwest Academy on Nanoelectronics sponsored by the Nanoelectronic Research Initiative and NIST and the Center for Low Energy Systems Technology, one of six centers supported by the STARnet phase of the Focus Center Research Program, a Semiconductor Research Corporation program sponsored by MARCO and DARPA.

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11:00am **2D+EM+MG+NS+SE+SM+SS+TF-ThM10 A Kinetic Study on the Adsorption of Polar (Water) and Non-Polar (Benzene) Molecules on CVD Graphene, Nilushni Sivapragasam, U. Burghaus, North Dakota State University**

The adsorption kinetics of water and benzene at ultrahigh vacuum conditions were studied. Two different chemical vapor deposited graphene samples (graphene/SiO₂ and graphene/Cu) were utilized. Different surface analytical techniques (Auger electron spectroscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy) were used to characterize the surface. Subsequently, a kinetics study - to understand the adsorption of water and benzene- using thermal desorption spectroscopy (TDS) was conducted. The TDS results revealed the hydrophobicity of water on graphene. However, the adsorption kinetics of water on graphene did not mimic the bare substrate, i.e., graphene is non-transparent for water adsorption. In contrast, graphene was transparent for benzene adsorption. Furthermore, the adsorption kinetics of both, water and benzene were substrate dependent.

11:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM11 Epitaxial Ultrathin MoSe₂ Layers Grown by Molecular Beam Epitaxy, Ming-Wei Chen, M.B. Whitwick, O. Lopez-Sanchez, D. Dumcenco, A. Kis, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland**

Two-dimensional transition metal dichalcogenides (TMDs) have attracted widespread attention recently, and the focus is specifically on ultrathin layers due to the strong spin-orbit coupling and direct band-gap transition of single-layers. The unique properties of various TMDs also enable the possibilities for future optoelectronic applications. However, the synthesis of TMDs with uniform large-area and high-quality still remains challenging. While chemical vapour deposition has been demonstrated as a promising technique, the complexity of chemical precursors and the lacking of *in-situ* observation technique strongly hinder the progress.

Here, We propose to use ultra-high vacuum molecular beam epitaxy (MBE) to grow MoSe₂ ultrathin layers, down to single-layer in a controllable way. Epitaxial MoSe₂ layers were successfully grown on different crystalline substrates via van der Waals epitaxy mechanism, benefited from the weak interlayer interaction and the lacking of dangling bonds. Reflection high energy electron diffraction (RHEED) was used to *in-situ* monitor the initial growth stage and revealed a clear transition of the streaks, demonstrating the formation of MoSe₂ layer. Sharp streaks were obtained in the growth end, with the streak spacing corresponding to MoSe₂ lattice constant, and no significant strain effect was observed. In order to demonstrate the validity of van der Waals epitaxy, different crystalline substrates with lattice mismatch up to 30 % have been tested. The epitaxial layers showed a smooth and uniform surface in atomic force microscopy, and the quality was further confirmed in Raman spectrum and transmission electron

microscopy. Furthermore, photoluminescence of the single-layer MoSe₂ showing a sharp peak of ~1.58 eV at room temperature demonstrates the direct band-gap feature and indicates the potentials of photovoltaic applications. In the end, the growth of two-dimensional van der Waals heterostructures has also been addressed and the results pave way for heterostructure studies.

In summary, molecular beam epitaxy has been proved to be a reliable route to grow large-area and high-crystalline transition metal chalcogenides, and is promising to facilitate the integration of other two-dimensional materials in the future.

11:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM12 A Two-Dimensional Oxide Quasicrystal, Stefan Förster, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany, J.I. Flege, Institute of Physics, University of Bremen, Germany, K. Meinel, R. Hammer, M. Trautmann, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany, J. Falta, Institute of Solid State Physics, University of Bremen, Germany, T. Greber, Physik-Institut, University of Zürich, Switzerland, W. Widdra, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany**

INVITED

With the recent discovery of the first oxide quasicrystal (QC) aperiodicity is entering the field of two-dimensional materials [1]. Aperiodicity means that the system exhibits long-range order as expressed by sharp diffraction spots but since the ordering follows an aperiodic function the system is lacking translational symmetry. We report here on the complex growth process of the oxide QC involving a high-temperature wetting process and periodic approximant structures.

The QC is derived from BaTiO₃ thin films on a hexagonal Pt(111) substrate and exhibits a sharp twelve-fold diffraction pattern [1]. Based on scanning tunneling microscopy the aperiodic atomic structure had been resolved [1]. It is formed by surface atoms arranged in forms of squares, triangles, and rhombi with a next-neighbour distance of 0.69 nm. In addition to this dodecagonal atomic arrangement, building blocks of squares, triangles, and rhombi are also found on (2+√3) and (2+√3)² larger scales indicating the characteristic self-similarity of an ordered QC [1]. The high-resolution STM measurements allow furthermore to identify atomic flips in the structure indicating lattice excitations in the quasicrystal called phasons. Using low-energy electron microscopy (LEEM) the preparation and the growth of the QC films on top of the hexagonal Pt(111) is monitored in all details from room temperature up to about 1200 K. LEEM shows that upon high-temperature annealing large 3DBaTiO₃ islands are formed with bare Pt(111)-(1x1) in between. At temperatures above 1020 K a wetting layer spreads on the free Pt area. This wetting process can be reversed by annealing in an oxygen atmosphere. In-situ LEEM measurements show that under these conditions the QC decays into small BaTiO₃ islands. The observed interface-driven formation of a 2D QC from a perovskite oxide in contact with a hexagonal substrate is expected to be a general phenomenon.

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Thursday Afternoon, October 22, 2015

2D Materials Focus Topic

Room: 212C - Session 2D+EM+MG+NS+SS+TF-ThA

Heterostructures of 2D Materials

Moderator: Stefan Förster, Martin-Luther-Universität Halle-Wittenberg, Michael Naguib, Oak Ridge National Laboratory

2:20pm **2D+EM+MG+NS+SS+TF-ThA1 Dielectrics Layer Deposition on 2D Materials by Functionalization with Polar Titanyl Phthalocyanine, JunHong Park**, UC San Diego, *S. Fahimpour*, University of Notre Dame, *I.J. Kwak*, UC San Diego, *H.C.P. Movva*, UT-Austin, *S. Vishwanath*, *H. Xing*, Cornell University, *S.K. Banerjee*, UT-Austin, *A.C. Seabaugh*, University of Notre Dame, *A.C. Kummel*, University of California at San Diego

Several novel designs for beyond CMOS devices have emerged using two-dimensional semiconductors. These devices require deposition of thin insulators on 2D semiconductors or between two sheets of 2D semiconductors. However, 2D semiconductors are nearly inert surfaces thereby making uniform nucleation of oxide growth challenging preventing scaling of the insulator thickness. A new technique has been developed to employ a monolayer of ordered metal phthalocyanines (MPc) on 2D semiconductors directly as a nucleation layer for growth of ALD dielectric. TiOPc monolayers were deposited on HOPG surfaces and WSe₂ by organic molecular beam epitaxy. TiOPc forms a monolayer with only few defects, and the crystal structure of monolayer has four-fold symmetry in a 1.6 x 1.6 nm grid on both HOPG and WSe₂. Observation of bright protrusions on each O-TiPc indicates that each O-TiPc in the monolayer is directed outward to vacuum. After exposure O-TiPc monolayer to 5 cycles ALD pulse (tri-methyl-aluminum (TMA)+H₂O), insulating aluminum oxide was deposited uniformly on TiOPc/HOPG. After formation of AlO_x on TiOPc/HOPG, the band gap of surface increases from 1.7 eV to 3.4 eV, while the conductance decreased. A metal-oxide-TiOPc-graphene capacitor has the lower thickness and the higher capacitance value than any reported graphene MOSCAPs. In the dual gated graphene FET with 40 cycles of AlO_x, TiOPc assisted AlO_x shows very low leakage current. Employing the TiOPc seeding layer also can be expanded to other TMD materials. The bottom gated WSe₂ FET was fabricated. On the bottom gated WSe₂ FET, the TiOPc monolayer was deposited, then 50 cycle of AlO_x was deposited via ALD. In this dual gated WSe₂ FET, the leakage current of the AlO_x is measured as ~0.05 pA/μm² at 0.5 VTG. As a control, 20 cycles of Al₂O₃, and 140 cycles of HfO₂ were deposited on bare WSe₂. The leakage current of the TiOPc assisted 50 cycle Al₂O₃ oxide is 3 orders of magnitude lower than HfO₂/Al₂O₃/WSe₂, consistent with a high nucleation.

2:40pm **2D+EM+MG+NS+SS+TF-ThA2 Direct Probing of the Electronic Structure of Bilayer Homo- and Hetero-Structures and Tracking their Evolution with Interlayer Twist-Angle, Nader Zaki, P. Yeh, W. Jin, R.M. Osgood, Jr.**, Columbia University

2D atomic layer materials such as graphene and transition-metal dichalcogenides such as MoS₂ have garnered much interest over the last few years due to their surprising electronic properties. For example, graphene possesses an exceptionally high mobility while monolayer MoS₂ possesses a direct bandgap with an exceptionally high light-matter interaction. One of the directions the 2D materials community is now pursuing is one in which these materials are combined together by way of vertical stacking in order to fabricate custom layered structures with potentially rich physics and unique device properties. Naturally, determining the electronic structure of these custom assembled structures is a necessary task to understanding their electronic behavior. While the electronic structure of the constituent materials have already been studied for monolayer form, the electronic structure of the stacked structures has only recently started to be deciphered. This talk will report on the direct determination of the electronic structure of two bilayer systems: twisted bilayer MoS₂ and twisted graphene/MoS₂. Using LEEM, μLEED, and μARPES, the stack quality, stack orientation, and stack electronic structure are directly probed and resolved with few μm and higher spatial resolution. To be discussed will be the evolution of the electronic structure with twist angle and its implications on the electronic properties of the respective homo- and hetero-structures.

3:00pm **2D+EM+MG+NS+SS+TF-ThA3 In Situ Microscopy on 2D Materials: Heterostructures, Nanostructures, Novel Materials Systems, Peter Sutter**, University of Nebraska - Lincoln **INVITED**

Two-dimensional (2D) materials, such as graphene, hexagonal boron nitride, and a family of metal dichalcogenides have fascinating properties

and show promise for applications. The broad exploration and use of these materials depends on the development of scalable synthesis methods, and of a fundamental understanding of their properties. I will discuss recent advances in understanding the synthesis, processing, and properties of 2D materials derived primarily from in-situ surface imaging.

In-situ microscopy provides the basis for creating complex heterostructures of different 2D materials, such as graphene and hexagonal boron nitride, and for studying atomically precise graphene nanostructures. Real-time imaging yields quantitative information on the growth and processing of new classes of 2D materials, such as metal dichalcogenide semiconductors. Finally, the combination of in-situ microscopy with synchrotron-based spectroscopy represents a unique approach for exploring the electronic band structure of 2D materials.

Our results illustrate that in-situ microscopy can be a powerful tool for realizing and probing the unique characteristics of two-dimensional materials.

4:00pm **2D+EM+MG+NS+SS+TF-ThA6 Direct Growth of Graphene/h-BN(0001) Multilayer Heterostructures for Novel Device Applications, S. Driver, D. Beatty, B. Olanipekun, S. Reid, Jeffry Kelber**, University of North Texas

We report the direct layer-by-layer growth of h-BN(0001) multilayers on Co(0001) by atomic layer epitaxy (ALE), and the direct growth of graphene multilayers on h-BN(0001) by molecular beam epitaxy (MBE). For the first time, this allows the growth of graphene/h-BN heterostructures with graphene and BN thicknesses controlled with atomic precision, and with all graphene and BN layers in azimuthal registry. Such control is a prerequisite for many proposed spintronic and electronic applications that emphasize charge or spin transport perpendicularly through the heterojunction. Further, the growth by direct, scalable methods without physical transfer, is essential for industrial development of such devices. h-BN(0001) multilayers have been deposited on Co(0001)/Al₂O₃(0001), using a BCl₃/NH₃ ALE process at 600 K. X-ray photoelectron spectroscopy (XPS) indicates B:N atomic ratios of 1:1 with negligible Cl contamination or reaction with the metallic substrate. Low energy electron diffraction (LEED) data indicate BN domain sizes of ~300 Å or greater, with the lattice in registry with that of the Co(0001) substrate. LEED data also indicate BN domains larger than those of the Co substrate, suggesting BN overgrowth of Co domain boundaries. The XPS-derived average BN film thickness scales linearly with the number of BCl₃/NH₃ cycles, and the lack of Co oxidation after ambient exposure of a BN bilayer indicates that these films are macroscopically continuous over the 1 cm x 1 cm sample size. Graphene formation on h-BN(0001) was achieved using MBE with a graphite rod source, with deposition carried out at 800 K. LEED data show the expected 6-fold LEED pattern in exact registry with that of the h-BN(0001)/Co(0001) substrate. XPS C 1s spectra indicate a C 1s binding energy near 284.5 eV and with the expected pi-to-pi* transition. A heterojunction consisting of ~3 monolayers (ML) graphene/3 ML h-BN on Co(0001) proved stable in vacuum to at least 1000 K, indicating the adaptability of this growth process to a variety of industrial applications. Other recent results indicate the adaptability of this process to other substrates, such as Ru(0001) or CoSi₂(111). These developments make possible a variety of spin filters, spin valves, and tunneling transistors proposed on the basis of close BN/graphene lattice matching, but not readily achievable with physically transferred films.

Acknowledgements: This work was supported by CSPIN, a MARCO/DARPA STARnet Center, under tasks 2381.001

and 2381.003, and by a UNT ROP grant. Peter Dowben and Jian-Ping Wang are acknowledged for stimulating and informative discussions.

4:20pm **2D+EM+MG+NS+SS+TF-ThA7 Al₂O₃ on Black Phosphorus by Atomic Layer Deposition: An in situ Interface Study, Hui Zhu, S. McDonnell, X. Qin, A. Azcatl, L. Cheng, R. Addou, J. Kim, UT-Dallas, P.D. Ye, Purdue University, R.M. Wallace, UT-Dallas**

Black phosphorus ("black-P") is considered to be an appealing 2D material because of its novel properties and potential application in few-layer transistor structures.^{1,2,3} However, a clear challenge in the implementation of black-P is the strong hydrophilic⁴ and oxidation⁵ reactions during device processing and thereafter. Thus, efficient isolation layers are necessary for black-P to preserve its electronic properties. Al₂O₃² or HfO₂⁶ dielectric layers deposited by atomic layer deposition (ALD) have been used as isolation layers in recent black-P transistors. In this work, three different samples oxidized by ambient air were investigated to understand the interfacial chemistry, and nucleation of atomic layer deposited Al₂O₃ on black-P using *in situ* X-ray photoelectron spectroscopy (XPS). This work suggests that exposing a sample that is initially free of phosphorus oxide to the ALD precursors does not result in detectable oxidation. However, when

the phosphorus oxide is formed on the surface prior to deposition, the black-P can react with both the surface adventitious oxygen contamination and the H₂O precursor at the deposition temperature of 200 °C. As a result, the concentration of the phosphorus oxide increases after both annealing and the atomic layer deposition process. The nucleation rate of Al₂O₃ on black-P is correlated with the amount of oxygen on samples prior to the deposition. The growth of Al₂O₃ follows a “substrate inhibited growth” behavior where an incubation period is required. *Ex situ* atomic force microscopy is also used to investigate the deposited Al₂O₃ morphologies on black-P where the Al₂O₃ tends to form islands on the exfoliated black-P samples.

This work was supported in part by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, the Center for Low Energy Systems Technology (LEAST), one of the six SRC STARnet Centers, sponsored by MARCO and DARPA, and the US/Ireland R&D Partnership (UNITE) under the NSF award ECCS-1407765.

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4:40pm **2D+EM+MG+NS+SS+TF-ThA8 Topological Winding Number Change and Broken Inversion Symmetry in a Hofstadter’s Butterfly**, *Marc Bockrath*, UC Riverside

Recently several research groups have demonstrated accurate placement of graphene on hexagonal BN (hBN) with crystallographic alignment. Due to the resulting superlattice formed in the graphene/hBN heterostructures, an energy gap, secondary Dirac Points, and Hofstadter quantization in a magnetic field have been observed. Using aligned layer transfer we are able to produce graphene/hBN heterostructures with ~1 degree alignment accuracy, and measure the transport properties of the resulting systems. We observe an additional π Berry’s phase shift in the magneto-oscillations when tuning the Fermi level past the secondary Dirac points, originating from a change in topological winding number from odd to even when the Fermi-surface electron orbit begins to enclose the secondary Dirac points. At large hole doping inversion symmetry breaking generates a distinct hexagonal pattern in the longitudinal resistivity versus magnetic field and charge density. This results from a systematic pattern of replica Dirac points and gaps, reflecting the fractal spectrum of the Hofstadter butterfly.

5:00pm **2D+EM+MG+NS+SS+TF-ThA9 Compliant Substrate Epitaxy: Au on MoS₂**, *Yuzhi Zhou, C. Daryl*, UC Berkeley

The heteroepitaxial growth of Au on MoS₂, a layered van der Waals bonded dichalcogenide, is analyzed. It is argued that the weak coupling between the layers in the dichalcogenides enables the first substrate layer to deform elastically almost independently from the substrate layers below, and hence enables epitaxial growth for a larger mismatch than might otherwise be expected. Linear, continuum elasticity theory and density functional theory are used to show that a {111} oriented Au film is the preferred over an {001} oriented Au film, despite the fact that the {111} orientation leads to a much higher elastic strain. During the initial stages of growth, the {111} orientation is favored over the {001} orientation due to its lower surface and interfacial energies. As the Au film grows thicker, the elastic relaxation of the first layer of the substrate leads to a reduction in the elastic energy of the growing film. This reduces the elastic energy difference between the {001} and {111} orientations enabling the {111} orientation to remain stable for all film thicknesses. This work is supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

5:20pm **2D+EM+MG+NS+SS+TF-ThA10 Direct Synthesis of 2D van der Waals Heterostructures**, *Judy Cha*, Yale University **INVITED**

Two-dimensional (2D) chalcogenides have gained renewed interest due to their interesting electrical properties such as topological insulator surface states in Bi₂Se₃ and hydrogen evolution catalytic activities in MoS₂. Our ability to thin them down to a single layer and their anisotropic bonding nature opens up possibilities for novel heterostructures where we can tailor

their electronic properties. I will present one-step, scalable heterostructure synthesis method to synthesize these chalcogenide nanostructures and examine their electronic transport properties. Intercalation into 2D materials will be considered as a novel way to design 2D heterostructures, in which the optical and electrical properties of the host 2D materials can drastically change. I will also discuss ways to control the alignment of molecular layers in these 2D chalcogenides, which exploits stress and strain built in the film during the growth. Electron tomography will be used to reconstruct the 3D structure of vertically oriented molecular layers in MoS₂ thin films. In the second part of the talk, I will present synthesis and electronic properties of SnTe topological crystalline insulator nanoplates. Although SnTe is cubic and not a layered material, large SnTe nanoplates expanding hundreds of microns in lateral dimension with ~100 nm in thickness are possible. I will discuss effects of substrates and growth conditions to promote thin film growth of non-layered materials.

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2D+EM+MG+NS+SE+SM+SS+TF-
ThM12, 10

Monazami, E.: NS+EN+MG+SS+TF-
WeA10, 7

Monfil-Leyva, K.: TF+2D+MG+NS-MoA7,
3

Movva, H.C.P.: 2D+EM+MG+NS+SS+TF-
ThA1, 11

Muñoz-Zurita, A.L.: TF+2D+MG+NS-
MoA7, 3

Myers-Ward, R.L.: TF+2D+MG+NS-MoA5,
3

— N —

Naghbi, S.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM1, 9

Naguib, M.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM3, **9**

Nath, A.: TF+2D+MG+NS-MoA5, 3

Nepal, N.: TF+2D+MG+NS-MoA5, 3

Nguyen, A.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM1, 9

Niemantsverdriet, H.J.W.:
NS+EN+MG+SS+TF-WeA9, 7

— O —

Ojeda-Durán, E.: TF+2D+MG+NS-MoA7, 3

Olanipekun, B.: 2D+EM+MG+NS+SS+TF-
ThA6, 11

- Osgood, Jr., R.M.: 2D+EM+MG+NS+SS+TF-ThA2, 11
— P —
 Park, J.H.: 2D+EM+MG+NS+SS+TF-ThA1, 11
 Pham, C.: TF+2D+MG+NS-MoA9, 3
 Pintauro, P.: TF+2D+MG+NS-MoA5, 3
 Preciado, E.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, 9
 Pruitt, B.L.: MN+MG-TuM1, 5; MN+MG-TuM3, 5
— Q —
 Qin, X.: 2D+EM+MG+NS+SS+TF-ThA7, 11
— R —
 Rahman, T.S.: NS+EN+MG+SS+TF-WeA1, 7
 Ramprasad, R.: MG+2D+MI+NS+TF-MoA3, 2
 Rappe, A.M.: MG+BI+MS+NS+TF-MoM8, 1
 Reid, S.: 2D+EM+MG+NS+SS+TF-ThA6, 11
 Reinke, P.: NS+EN+MG+SS+TF-WeA10, 7
 Reyes, P.: NS+EN+MG+SS+TF-WeA3, 7
 Robinson, J.A.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM6, 9
 Robinson, Z.R.: TF+2D+MG+NS-MoA5, 3
 Roozeboom, C.: MN+MG-TuM3, 5
 Ruzic, D.N.: MG+2D+MI+NS+TF-MoA5, 2
— S —
 Sadeghipour, E.: MN+MG-TuM3, 5
 Saidi, W.A.: MG+BI+MS+NS+TF-MoM8, 1
 Saldana-Greco, D.: MG+BI+MS+NS+TF-MoM8, 1
 Seabaugh, A.C.: 2D+EM+MG+NS+SS+TF-ThA1, 11
 Self, E.: TF+2D+MG+NS-MoA5, 3
 Shacham-Diamand, Y.: MN+MG-TuM4, 5
 Shafai, G.: NS+EN+MG+SS+TF-WeA1, 7
 Shchelkanov, I.A.: MG+2D+MI+NS+TF-MoA5, 2
 Shukla, N.: NS+EN+MG+SS+TF-WeA11, 8
 Shumlas, S.L.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM2, 9
 Sim, J.Y.: MN+MG-TuM3, 5
 Simmons, J.G.: TF+2D+MG+NS-MoA1, 2
 Singh, B.: MG+2D+MI+NS+TF-MoA6, 2
 Sivapragasam, N.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM10, 10
 Smith, C.: MN+MG-TuM5, 5
 Stiff-Roberts, A.D.: TF+2D+MG+NS-MoA2, 2
 Strongin, D.R.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM2, 9
 Sutter, P.W.: 2D+EM+MG+NS+SS+TF-ThA3, 11
— T —
 Thenuwara, A.C.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM2, 9
 Trautmann, M.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM12, 10
 Tsipas, P.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM5, 9
 Tsoutsou, D.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM5, 9
— V —
 Van der Boom, M.E.: NS+EN+MG+SS+TF-WeA7, 7
 Van Volkinburg, K.: MN+MG-TuM4, 5
 Vernisse, L.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM2, 9
 Vishwanath, S.: 2D+EM+MG+NS+SS+TF-ThA1, 11
 von Son, G.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, 9
— W —
 Wallace, R.M.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM6, 9; 2D+EM+MG+NS+SS+TF-ThA7, 11
 Wang, J.K.: TF+2D+MG+NS-MoA10, 4
 Washington, G.N.: MN+MG-TuM4, 5
 Wen, X.: NS+EN+MG+SS+TF-WeA9, 7
 Westwood-Bachman, J.N.: MN+MG-TuM12, 6
 Wheeler, V.D.: TF+2D+MG+NS-MoA5, 3
 Whitwick, M.B.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM11, 10
 Widdra, W.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM12, 10
— X —
 Xenogiannopoulou, E.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM5, 9
 Xing, H.: 2D+EM+MG+NS+SS+TF-ThA1, 11
— Y —
 Yang, D.: NS+EN+MG+SS+TF-WeA11, 8
 Ye, P.D.: 2D+EM+MG+NS+SS+TF-ThA7, 11
 Yeh, P.: 2D+EM+MG+NS+SS+TF-ThA2, 11
— Z —
 Zaki, N.: 2D+EM+MG+NS+SS+TF-ThA2, 11
 Zhou, Y.: 2D+EM+MG+NS+SS+TF-ThA9, 12
 Zhu, H.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM6, 9; 2D+EM+MG+NS+SS+TF-ThA7, 11
 Zurek, E.: MG+BI+MS+NS+TF-MoM10, 1