2D Materials Focus Topic
Room: 15 - Session 2D+EM+MI+MN-MoM

Properties of 2D Materials including Electronic, Magnetic, Mechanical, Optical, and Thermal Properties
Moderator: Andrey Turchanin, Friedrich Schiller University Jena, Germany

8:20am **2D+EM+MI+MN-MoM1 Spontaneous Mechanical Buckling in Two-Dimensional Materials: A Power Source for Ambient Vibration Energy Harvesters**, ***Paul Thibado***, *P. Kumar*, *S. Singh*, University of Arkansas

Internet-of-Things (IoT) is projected to become a multi-trillion-dollar market, but most applications cannot afford replacing batteries on such a large scale, driving the need for battery alternatives.

We recently discovered that freestanding graphene membranes are in perpetual motion when held at room temperature [1-3]. Surprisingly, the random up-down motion of the membrane does not follow classical Brownian motion, but instead is super-diffusive at short times and sub-diffusive at long times. Furthermore, the velocity probability distribution function is non-Gaussian and follows the heavy-tailed Cauchy-Lorentz distribution, consistent with Levy flights.

Molecular dynamics simulations reveal that mechanical buckling is spontaneously occurring, and that this is the mechanism responsible for the anomalous movement. Bucking in this system occurs when the local material suddenly flips from concave to convex.

The higher kinetic energy associated with this motion is derived from the surrounding thermal waste heat, and it may be converted into an electrical current and used as the active component of small power generators known as ambient vibration energy harvesters.

References:

[1] P. Xu, M. Neek-Amal, S.D. Barber, J.K. Schoelz, M.L. Ackerman, P.M. Thibado, A. Sadeghi, and F.M. Peeters, Nature Comm. **5**, 3720 (2014).

[2] M. Neek-Amal, P. Xu, J.K. Schoelz, M.L. Ackerman, S.D. Barber, P.M. Thibado, A. Sadeghi, and F.M. Peeters, Nature Comm. **5**, 4962 (2014).

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8:40am **2D+EM+MI+MN-MoM2 Topological Toughening of Graphene and other 2D Materials**, ***Bo Ni***, *H.J. Gao*, Brown university

It has been claimed that graphene, with the elastic modulus of 1 TPa and theoretical strength as high as 130 GPa, is the strongest material. However, from an engineering point of view, it is the fracture toughness that determines the actual strength of materials, as crack-like flaws (i.e., cracks, holes, notches, corners, etc.) are inevitable in design, fabrication and operation of practical devices and systems. Recently, it has been demonstrated that graphene has very low fracture toughness, in fact close to that of ideally brittle solids. These findings have raised sharp questions and are calling for efforts to explore effective methods to toughen graphene. Recently, we have been exploring the potential use of topological effects to enhance the fracture toughness of graphene. For example, it has been shown that a sinusoidal graphene containing periodically distributed disclination quadrupoles can achieve a mode I fracture toughness nearly twice that of pristine graphene. Here we report working progresses on further studies of topological toughening of graphene and other 2D materials. A phase field crystal method is adopted to generate the atomic coordinates of material with specific topological patterns. We then perform molecular dynamics simulation of fracture in the designed samples, and observe a variety of toughening mechanisms, including crack tip blunting, crack trapping, ligament bridging, crack deflection and daughter crack initiation and coalescence.

9:00am **2D+EM+MI+MN-MoM3 Ferroelectric Domain Control of Photoluminescence in Monolayer WSe_2 / PZT Hybrid Structures**, ***Berry Jonker***, *C.H. Li*, *K.M. McCreary*, Naval Research Laboratory

Single monolayer transition metal dichalcogenides (TMDs) exhibit exceptionally strong photoluminescence dominated by a combination of distinct neutral and charged exciton contributions. The dielectric screening is very low due to their two-dimensional character relative to bulk material, and their properties are thus strongly affected by their immediate environment. Because the exciton and trion binding energies are very large (~ 600 meV and ~30 meV, respectively), these characteristic emission features persist to room temperature. The samples were fabricated by mechanically transferring large area monolayer WS_2 grown by a CVD process onto 100 nm thick lead zirconium titanate (PZT) films on a conducting *n*-type strontium titanate wafer. We show here that the surface charge associated with ferroelectric domains patterned into the PZT film with a conductive atomic force microscope laterally control the spatial distribution of neutral and charged exciton populations in the adjacent WS_2 monolayer [1]. This is manifested in the intensity and spectral composition of the photoluminescence measured in air at room temperature from the areas of WS_2 over a ferroelectric domain with polarization dipole pointed either out of the surface plane or into the surface plane. The photoluminescence from areas of the WS_2 over up polarization domains in the PZT are dominated by neutral exciton emission, while those over down domains are dominated by trion emission, consistent with the corresponding charge produced by the domains at the WS_2 / PZT interface. The hysteretic character of ferroelectric materials means that the TMD properties can be selectively reconfigured in a nonvolatile manner by changing the state of the ferroic substrate. This approach enables spatial modulation of TMD properties with a spatial resolution determined by the polarization domains in the underlying ferroelectric layer, with the potential for fabrication of lateral quantum dot arrays or *p-n* junctions in any geometry of choice.

[1] C.H. Li, K.M. McCreary and B.T. Jonker, *ACS Omega* 1, 1075 (2016).

This work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #AOARD 14IOA018-134141.

9:20am **2D+EM+MI+MN-MoM4 Mechanical Instability-driven Architecturing of Atomically-thin Materials**, ***SungWoo Nam***, University of Illinois at Urbana-Champaign

Mechanical deformations, such as buckling, crumpling, wrinkling, collapsing, and delamination, are usually considered threats to mechanical integrity which are to be avoided or reduced in the design of materials and structures. However, if materials systems and applied stresses are carefully controlled, such mechanical instabilities can be tailored to deterministically create functional morphologies that can enable powerful new functions. In particular, in atomically-thin material systems with ultralow bending stiffness, such as graphene, mechanical deformations enable new structural properties and device-level functionalities which surpass the limits of bulk material systems. In this talk, I will present our manufacturing technique on controlled deformation and straining of atomically-thin materials, and the emergent materials properties and applications of such deformed and strained atomically-thin materials. First, I will introduce shrink-manufacturing approaches to enable controlled deformation of atomically-thin materials. Second, I will introduce a wide range of new material properties enabled by the new class of 'architectured atomically-thin materials'. I will discuss the surface plasmonics enabled by crumpled topographies of graphene and will further discuss shape reconfigurability which opens the door to tunable plasmonic resonance of crumpled graphene. In addition, I will share our ongoing research efforts on strained superlattice for the modulation of electronic properties. Third and last, I will present our work on adaptive/conformal and multifunctional electronics based on mechanically deformed atomically-thin materials. Our optoelectronic sensor is based exclusively on graphene and transforms the two dimensional material into three dimensional (3D) crumpled structures. This added dimensionality enhances the photoabsorption of graphene by increasing its areal density with a buckled 3D structure, which simultaneously improves device stretchability and furthermore enables strain-tunable photoresponsivity. Our approach to manufacturing architectured atomically-thin materials offers a unique avenue for enabling new materials properties and engineering of advanced device functions.

9:40am **2D+EM+MI+MN-MoM5 Excitons and Exciton Complexes in Transition Metal Dichalcogenide Monolayers**, ***Mark Hybertsen***, Brookhaven National Laboratory **INVITED**

Ultra-thin semiconductor crystals, realized from transition metal dichalcogenides and other Van der Waals materials, exhibit fascinating optical properties. In the limit of a single monolayer of material, the Coulomb interactions between the optically excited electrons and holes are particularly strong and specifically deviate in functional form from that familiar from bulk semiconductors ($1/\varepsilon r$) [1]. In combination with the reduced dimensionality, the resultant interaction effects are an order of magnitude stronger than those that were previously observed in quantum well structures realized in epitaxially grown multilayers. The lowest energy excitations created by optical excitation are bound electron-hole pairs (excitons). The binding energy is on the 0.5 eV scale and the ladder of bound state energies observed deviate significantly from the spectrum predicted by the conventional hydrogenic model [2]. In the presence of excess carriers, the excitons also form a bound complex with either an excess electron or hole (trions) [1]. As the density of optically excited excitons is increased, pairs of bound excitons form (biexcitons), with a clear spectroscopic signature [3]. All of these characteristics of excitons and exciton complexes in transition metal dichalcogenides can be understood directly from the strong and modified form of the Coulomb interaction, including both the role of the environment and the impact of the intrinsic screening response of the material. In particular, a model Hamiltonian can be fully determined from microscopic inputs and solved for the properties of the observed excitons and associated complexes. Variational solutions are semiquantitative while supplying insight. A Monte Carlo approach solves the model Hamiltonian numerically exactly and gives quantitative relationships among the exciton and exciton complex binding energies [4]. Extensions of these approaches to understand excited states in more complex combinations of such layered materials will also be discussed.

Work performed in part at the CFN, which is a U.S. DOE Office of Science Facility, at BNL under Contract No. DE-SC0012704 and with resources from NERSC under Contract No. DE-AC02-05CH11231.

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[3] Y. You, X.-X. Zhang, T. C. Berkelbach, M. S. Hybertsen, D. R. Reichman, and T. F. Heinz, Nat. Phys. **11**, 477 (2015).

[4] M. Z. Mayers, T. C. Berkelbach, M. S. Hybertsen, and D. R. Reichman, Phys. Rev. B **92**, 161404 (2015).

11:00am **2D+EM+MI+MN-MoM9 Mechanical Properties of Polycrystalline and Defective Graphene**, ***Joseph Gonzales***, *I.I. Oleynik*, *J.T. Willman*, University of South Florida, *R. Perriot*, Los Alamos National Laboratory

Experimental investigation of mechanical properties indicates that the polycrystalline graphene grown by chemical vapor deposition is as strong as pristine. Recent experiments involving nanoindentation of graphene have also demonstrated counterintuitive increasing of Young's modulus with increasing concentrations of point defects. Using accurate description of interatomic interactions provided by novel screened environment-dependent bond order, (SED-REBO) potential, we performed large-scale molecular dynamics investigations of mechanical properties of polycrystalline and defective graphene samples under conditions mimicking nano-indentation AFM experiments. The atomically resolved characterization of the stress and strain distributions under indenter are used to understand fundamental mechanisms of graphene strength and failure. The breaking strength, the crack initiation and propagation are investigated as a function of the grain boundary structure, grain size distribution, concentration of point defects as well as the position of the indenter in respect to these extended and point defects.

11:20am **2D+EM+MI+MN-MoM10 Properties of Single Layer Transition Metal Dichalcogenides Grown by Van der Waals Epitaxy**, ***Matthias Batzill***, University of South Florida **INVITED**

It is well documented that the electronic properties of transition metal dichalcogenides (TMDs) vary as their dimensions are reduced to a single layer. Also, variations depending on the substrate have been reported. In our studies we grow single- to few- layers of TMDs by molecular beam epitaxy on van der Waals substrates (mainly HOPG or bulk-MoS_2). Despite the weak interactions between the monolayer and the substrate the film grows rotational aligned so that a film exhibits a single crystal orientation. This enables for example electronic structure characterization by angle resolved photoemission spectroscopy. The versatile growth procedure allows us to characterize many materials systems. First we discuss the role of the substrate for semiconducting TMDs. We study the electronics structure variation for $MoSe_2$ grown on another TMD (MoS_2) and compare it with that grown on HOPG. While the band dispersion of $MoSe_2$ on HOPG resembles the expectations for free-standing $MoSe_2$ it is modified for $MoSe_2/MoS_2$ due to interlayer hybridization of the chalcogen p-orbitals. A big advantage of MBE growth in vacuum is that it enables the synthesis and study of more reactive systems – like most metallic TMDs. Thus, in the second part of this talk we investigate the properties of single layer $TiSe_2$. $TiSe_2$ is an unconventional charge density wave (CDW) material whose charge density wave transition has been associated with an excitonic insulator phase. Such an excitonic insulator is formed spontaneously if the excitonic binding energy exceeds the band gap and thus formation of excitons may become the ground state. By scanning tunneling spectroscopy we observe significant increase in the CDW-band gap opening at the Γ-point for the monolayer compared to few-layer materials. Furthermore, the opening of the gap varies with the substrate material, consistent with expectations for excitonic binding energies. Interestingly, we observe coherence peaks in the tunneling spectra below 50 K suggesting the formation of an excitonic condensate.

Actinides and Rare Earths Focus Topic
Room: 22 - Session AC+MI+SA+SU-MoM

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

Moderator: Tomasz Durakiewicz, Los Alamos National Laboratory

8:20am **AC+MI+SA+SU-MoM1 Magnetic and Transport Characteristics in the Uranium Intermetallic Compounds with the $HoCoGa_5$-type Structure**, ***Yoshinori Haga***, Japan Atomic Energy Agency, Japan **INVITED**

Physical properties of actinides compounds are mainly dominated by the 5f electrons behavior. The spatial extent of the 5f wave function and resulting hybridization with the neighboring atoms lead to itinerant characters. On the other hand, well isolated 5f electrons carry magnetic moment. Competition between those two characteristics often bring about peculiar electronic properties. Among a series of actinides compounds, so-called 115 compounds crystallizing in the tetragonal $HoCoGa_5$-type structure have extensively been studied because of unusual correlated electronic states, including heavy effective mass of conduction electrons, magnetic orderings and heavy fermion superconductivity. Those compounds are also good cases to study electronic transport properties in detail because of availability of extremely high quality samples. Among them, we discuss electronic properties of $URhX_5$ (X = Ga and In). While $URhIn_5$ orders antiferromagnetically at fairly high tempearture 98 K, isostructural and formally isoelectronic analogue $URhGa_5$ is a nonmagnetic semimetal[1,2,3]. Detailed transport measurements as well as the de Haas-van Alphen experiment revealed Fermi surface characteristics. We discuss origin of magnetism of uranium 5f electrons and its relationship between superconductivity realized in Pu-analogues.

[1] Y. Matsumoto et al., Phys. Rev. B 88, 045120 (2013).

[2] S. Ikeda et al., Physica B 359-361, 1039 (2005).

[3] Y. Matsumoto et al, JPS Conf. Proc. 3, 011097 (2014).

9:00am **AC+MI+SA+SU-MoM3 Magnetic Structures of Layered U_nRhIn_{3n+2} Materials**, ***Attila Bartha***, *M. Klicpera*, Charles University, Prague, Czech Republic, *P. Čermák*, Forschungszentrum Juelich GmbH, Germany, *B. Ouladdiaf*, Institut Laue Langevin, France, *P. Javorský*, *J. Custers*, Charles University, Prague, Czech Republic

Materials of reduced dimensionality appear in many contemporary fields of research and technology, because they encompass a wide variety of interesting electronic phenomena. For instance carbon can be prepared in 3D (diamond), quasi-2D (graphite), 2D (graphene) or 1D (carbon nanotubes). All of these structures have distinct electronics. Diamond is an insulator. Graphene is semimetal. However, when the dimensionality is increased by putting several graphene layers together (eventually making graphite), the resulting band structure moves to that of a more trivial metal. Another example is high temperature superconductors being quasi-2D materials as well.

The role of dimensionality in *f*-electron systems has been mainly discussed in the context of quantum phase transitions and related phenomena. The series $Ce_nT_mIn_{3n+2m}$(n=1, 2; m=0, 1, 2; T=transition metal) of layered compounds, which can be viewed as m TIn_2–layers alternating with n–layers of $CeIn_3$ along the *c*-axis, has been extensively investigated. $CeIn_3$ is cubic (3D) and orders antiferromagnetically (AFM) at T_N = 10.2 K [1] with a propagation vector $\boldsymbol{k}$ = (0.5, 0.5, 0.5) [2]. Under hydrostatic pressure superconductivity appears with highest T_c = 0.3 K at p = 2.5 GPa. In $CeRhIn_5$, the anisotropic crystal structure leads to an incommensurate magnetic structure described with $\boldsymbol{k}$ = (0.5, 0.5, 0.297). The AFM order is reduced (T_N = 3.8 K) while superconductivity is supported, T_c increases to 1.9 K at p = 1.77 GPa [3-4].

We report on the magnetic structures of $URhIn_5$ and U_2RhIn_8, two new members of this intriguing $R_nT_mX_{3n+2m}$(R= Lanthanide, Actinide, X = In, Ga) family of compounds. Neutron diffraction measurements were performed on structurally well-defined single crystals. Both, $URhIn_5$ and U_2RhIn_8, adopt the tetragonal Ho_nCoGa_{3n+2}-type structure (P4/*mmm*) typical for this group of compounds. $URhIn_5$ orders antiferromagnetically below T_N = 98 K. The propagation vector equals $\boldsymbol{k}$ = (0.5, 0.5, 0.5) and we obtained a value of 1.65 μ_B/U^{3+} for the size of the ordered magnetic moment. The antiferromagnetic transition temperature of U_2RhIn_8 is higher yielding 117 K. We found that the magnetic structure can be described by propagation vector $\boldsymbol{k}$ = (0.5, 0.5, 0). The respective ordered magnetic moment amounts 1.7 μ_B/U^{3+}. In both materials the ordered magnetic moments are aligned along the tetragonal *c*-axis. Comparison with isostructural compounds and general conclusions for the series will be presented.

[1] C. Pfleiderer, Rev. Mod. Phys. 81 (2009) 1551

[2] A Benoit *et al*., Solid State Commun. 34 (1980) 39

[3] H. Shishido *et al.* J. Phys. Soc. Jpn. Vol. 71 Suppl. (2002) 276

[4] H. Hegger *et al.,* Phys. Rev. Lett. 84 (2000) 4986

9:20am **AC+MI+SA+SU-MoM4 U_3Si_2 – Physical Properties and Resistance to Hydrogen**, ***Silvie Maskova***, Charles University, Prague, Czech Republic, *K. Miliyanchuk,* Ivan Franko National University of Lviv, Lviv, Ukraine, *S. Middleburgh,* Westinghouse Electric Sweden AB, Vasteras, Sweden, *L. Havela*, Charles University, Prague, Czech Republic

U_3Si_2 (tetragonal structure with the space group of *P*4/*mbm* and two different U-positions, U1 and U2, in the unit cell) is considered to be promising material (due to its high density of uranium) as an accident-tolerant nuclear fuel [1] with rather high melting point (1938 K) indicating a high thermodynamic stability. From this point of view, it is very important to study its resistance to oxygen or hydrogen, as it can significantly influence the integrity of the material. U_3Si_2 was reported to oxidize at elevated temperatures [2].

We studied the H absorption and concomitant changes of basic electronic properties. We found that U_3Si_2 reversibly absorbs hydrogen (H can be released again by heating up to approx. 700 K) to the level of approximately 1.8 H/f.u., i.e. yielding $U_3Si_2H_{1.8}$. The H absorption proceeds at very low H pressures (kPa range) already, resulting in 10 % volume expansion. The temperature-induced desorption experiment showed that the hydrogen atoms are located in one specific position only. The crystal structure arrangement suggests that two different positions should be considered - U_3Si tetrahedra (similar to U_3T tetrahedra in U_2T_2X compounds [3] crystallizing in an ordered ternary derivative of the U_3Si_2 structure) and a split position in the U_6 octahedra consisting of 4 U1 and 2 U2 atoms (H atom shifts from the central position into the tetrahedra formed by 2 U1 and 2 U2 atoms. As H generally does not occupy two adjacent tetrahedra, we can assume only two from the 4 tetrahedra occupied). The later was confirmed as more plausible option by ab-initio calculations using Vienna Ab-initio Simulation Package (VASP) with the PBE-GGA exchange correlation.

Magnetic studies of U_3Si_2 confirmed that it is a Pauli paramagnet, as reported previously [4]. The volume expanded hydride reveals a Curie-Weiss behavior and a weak and inhomogeneous ferromagnetism arising gradually below T = 100 K. The low-temperature specific heat of $U_3Si_2H_{1.8}$ shows an upturn and a dramatic enhancement of the Sommerfeld coefficient of electronic specific heat γ, which reaches 440 mJ/mol f.u. K^2 (γ = 88 mJ/mol f.u. K^2 for U_3Si_2).

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9:40am **AC+MI+SA+SU-MoM5 Understanding Surface Chemistry of f-element Oxides using First-principle Methods**, ***Ping Yang***, Los Alamos National Laboratory **INVITED**

Interfacial chemistry for f-element materials is critical for nuclear waste management and to address the environmental concerns associated with actinides. Cerium is often used as a surrogate for more radioactive actinide elements for thorough characterization using advanced spectroscopic techniques. Herein, we will present recent progress in characterizing interfacial interactions of ligands with CeO_2 and ThO_2 in both surface and nanoparticle forms. We will demonstrate how the synergy between theory and experiment has accelerated the progress in this field. The theoretical results are validated by spectroscopic characterizations. A better molecular-level understanding of the interfacial chemistry including coordination, energetics and reaction mechanisms will pave the way to a better strategy for waste management and environment remediation.

10:40am **AC+MI+SA+SU-MoM8 Inelastic X-ray Scattering Study of the Crystal Dynamics of Neptunium and Uranium Dioxide**, ***Roberto Caciuffo***, European Commission, Joint Research Centre, Karlsruhe, Germany, *P. Maldonado,* Uppsala University, Sweden, *L. Paolasini,* European Synchrotron Radiation Facility, France, *P.M. Oppeneer,* Uppsala University, Sweden, *T.R. Forrest*, European Synchrotron Radiation Facility, France, *A. Prodi,* Consiglio Nazionale delle Ricerche, Italy, *N. Magnani*, European Commission, Joint Research Centre, Karlsruhe, Germany, *A. Bosak,* European Synchrotron Radiation Facility, France, *G.H. Lander*, European Commission, Joint Research Centre, Karlsruhe, Germany **INVITED**

The energy-wavevector dispersion relations for normal modes of vibration propagating along high-symmetry lines in NpO_2 and UO_2 have been determined by measuring the coherent one-phonon scattering of X-rays from single-crystal specimens with mass varying from a few µg to ~1 mg. The inelastic X-ray scattering (IXS) experiments were carried out using the ID28 beamline at ESRF with an incident energy E=17.794 keV. The results are compared against *ab initio* phonon dispersion simulations computed within the first-principles density functional theory in the generalized gradient approximation plus Hubbard U correlation (GGA+U) approach, taking into account third-order anharmonicity effects in the quasiharmonic approximation.

In the case of NpO_2, the sample of dimension of $0.4x0.3x0.3mm^3$ was oriented with the specular direction along the (100) crystal axis and the (011) axis in the scattering plane. We have investigated different Brillouin zones in order to optimize the inelastic structure factor for the different optic branches. Optic phonons arise mainly from oxygen vibration modes and are very weak. Thermal expansion, heat capacity, thermal conductivity, phonon linewidth, and thermal phonon softening are calculated and compared with experimental data available for both NpO_2 and UO_2 [1]. We show that optical phonons contribute significantly to the heat transport due mainly to their large velocities and short lifetimes. Compared with UO_2, the main differences in the phonon density of states of NpO_2 are a softening of the optical modes and an increase of the peak centred around 55 meV, whereas the acoustic modes in NpO_2 are shifted to higher frequencies. The calculated value at 0 K of the bulk modulus in NpO_2 is in agreement with the experimental value and slightly smaller than the one determined by high-pressure X-ray diffraction for UO_2. NpO_2 has a smaller thermal conductivity than UO_2, at least in the temperature range 600 to 1000 K for which experimental values are available.

The lattice dynamics of UO_2 have been extensively investigated by neutron scattering both at low and high temperature. In this study we focussed our attention to the low temperature region, searching for vibronic contributions to the vibrational-magnetic-quadrupolar mixed modes that appear in UO_2 because of magnetoelastic and multipolar superexchange interactions. The situation is cleaner than with neutrons, as the latter see both magnons and phonons – the IXS spectra just the phonons. This observation opens a new window on these “hidden excitations”, which drive much of the physics of UO_2.

[1] P. Maldonado *et al.,* Phys Rev B **93**, 144301 (2016)

11:20am **AC+MI+SA+SU-MoM10 Emergent Phenomena in 4f Heavy-Fermion Systems: from Bulk to Thin-Films**, ***Priscila Rosa***, Los Alamos National Laboratory **INVITED**

The interplay between magnetism and unconventional superconductivity in bulk materials has been one of the central topics in condensed matter physics for the past 40 years. In particular, the family of compounds Ce*M*In$_5$ (M = Co, Rh, Ir) provides an ideal platform for such investigation due to the small energy scales involved, and the high sample quality. In this talk, I will first discuss novel insights provided by substitution studies in bulk $CeRhIn_5$ under pressure. I will then present recent efforts to fabricate hybrid superlattices consisting of alternating superconducting $CeCoIn_5$ and antiferromagnetic $CeRhIn_5$.

Applied Surface Science Division
Room: 13 - Session AS+BI+MI-MoM

Practical Surface Analysis: Getting the Most Out of Your Analysis using Complementary Techniques

Moderators: Mark Engelhard, EMSL, Pacific Northwest National Laboratory, Michaeleen Pacholski, The Dow Chemical Company

8:20am **AS+BI+MI-MoM1 Obtaining Complete Characterisation of Core-shell Nanoparticle Structure and Composition *via* the use of Complementary Techniques**, ***David Cant***, *C. Minelli*, National Physical Laboratory, UK, *K. Sparnacci*, Università degli Studi del Piemonte Orientale, Italy, *W. Unger*, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany, *A. Hermanns*, Bundesanstalt für Materialforschung und -prüfung (BAM), *W.S.M. Werner, H. Kalbe*, TU Wien, Austria, *R. Garcia-Diez, C. Gollwitzer, M. Krumrey*, Physikalisch-Technische Bundesanstalt, Germany, *A.G. Shard*, National Physical Laboratory, UK

Core-shell nanoparticles are commonly used in a variety of applications, including medicine, catalysis, optoelectronics, and others. Accurate identification of core-shell nanoparticle structure and morphology is an important challenge to overcome before such nanoparticles can be effectively utilised. This is not necessarily a trivial obstacle, as no single characterisation technique can accurately identify every possible peculiarity of structure or composition that may exist.

For example, characterisation methods that observe bulk properties, such as differential centrifugal sedimentation (DCS), thermogravimetric analysis (TGA), or techniques based on observation of Brownian motion such as dynamic light scattering (DLS) may be unable to distinguish particles with a standard core-shell morphology from those with the same core and shell masses, but with an uneven shell, or where the core and shell have merged to form a homogenous particle.

Similarly, surface sensitive techniques which analyse a population of particles, such as x-ray photoelectron spectroscopy (XPS) or small angle x-ray scattering (SAXS), may be able to provide information on shell thicknesses in standard core-shell particles and distinguish them from particles with an uneven shell or a homogenous particle, but may have difficulty distinguishing homogeneity from an uneven shell or off-centred core.

Techniques that allow observation of individual particles, such as electron microscopy, may be able to clearly show the structure, but are rarely able to provide any in-depth quantification of the composition. As such it is necessary to use a careful selection of appropriate techniques to fully characterise any given nanoparticle system. To illustrate these issues, two polymeric core-shell nanoparticle systems have been characterised, both consisting of a Hyflon® core coated in varying thicknesses of either PMMA or polystyrene. These systems are nominally very similar, but differ notably in structure. The results from several different characterisation techniques (XPS, SAXS, DCS, TGA, DLS, and SEM.) were compared in order to demonstrate the difference in information provided by each and obtain a full understanding of both types of nanoparticle.

9:00am **AS+BI+MI-MoM3 Correlative Microscopy based on Secondary Ion Mass Spectrometry for High-Resolution High-Sensitivity Nano-Analytics**, ***Tom Wirtz***, *J.-N. Audinot, D.M.F. Dowsett, S. Eswara*, Luxembourg Institute of Science and Technology (LIST), Luxembourg **INVITED**

Development of innovative characterization tools is of paramount importance to advance the frontiers of science and technology in nearly all areas of research. In order to overcome the limitations of individual techniques, correlative microscopy has been recognized as a powerful approach to obtain complementary information about the investigated materials. High-resolution imaging techniques such as Transmission Electron Microscopy (TEM) or Helium Ion Microscopy (HIM) offer excellent spatial resolution. However, the analytical techniques associated with TEM such as Energy Dispersive X-ray spectroscopy (EDX) or Electron Energy-Loss Spectroscopy (EELS) are inadequate for the analysis of (i) isotopes, (ii) trace concentrations (< 0.1 at. % or < 1000 ppm) and (iii) light elements (H, Li, B). Likewise, for the case of HIM, until recently there was no direct possibility to perform elemental mapping because sub-30 keV He$^+$ or Ne$^+$ ion irradiation do not excite X-ray emission. Secondary Ion Mass Spectrometry (SIMS), on the other hand, is an extremely powerful technique for analysing surfaces owing in particular to its excellent sensitivity (detection limits down to the ppb are possible, so that SIMS can be used to detect both major and trace elements), high dynamic range (a same signal can be followed over several orders of magnitude), high mass resolution and ability to differentiate between isotopes.

In order to combine the high spatial resolution of TEM and HIM with the analytical sensitivity of SIMS, we developed integrated TEM-SIMS [1,2] and HIM-SIMS [2-4] instruments. The main advantage of this in-situ correlative approach is its capability to analyse the same area of interest of any sample without need of transferring the sample from one instrument to another one, which would result in a number of artefacts ranging from surface contamination to issues with localizing exactly the same ROIs. Moreover, the integrated approach allows fast and multiple interlacing between the different imaging and analysis modes.

In this talk, we will first introduce the TEM-SIMS and HIM-SIMS instruments and discuss their performance characteristics. We will then present a number of examples taken from various fields of materials science and life science to show the powerful correlative microscopy possibilities enabled by these new in-situ methods.

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9:40am **AS+BI+MI-MoM5 New Insights on Layered Polymer Systems, Polymer Networks and Polymerization in Defined Geometries by Combining Surface Analysis with Depth Profiling using ToF-SIMS and XPS as Analytical Tools**, ***Sven Steinmüller***, Institute for Applied Materials, Karlsruhe Institute of Technology, Germany, *A. Llevot*, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Germany, *D. Moock*, Institute for Applied Materials, Karlsruhe Institute of Technology, Germany, *B. Bitterer*, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Germany, *F. Cavalli*, Institute for Biological Interfaces, Karlsruhe Institute of Technology, Germany, *S. Hurrle*, Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Germany, *M. Bruns*, Institute for Applied Materials, Karlsruhe Institute of Technology, Germany

Surface analytical characterization of polymers is still a tough topic if precise information are favored. Especially for characterization of stepwise layered systems and for studying reaction rates and composition of network formation or to confirm polymerization within defined geometries a lot of techniques are not sensitive enough to fulfill the desired degree of precision and resolution. Within the recently installed Cooperate Research Center “SFB 1176” at KIT (Molecular Structuring of Soft Matter), a high degree of precision is necessary to qualitatively and quantitatively confirm the defined structures achieved during the polymer syntheses. Here a new surface analysis approach combining X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) including Ar cluster ion sputter depth profiling for three dimensional systems is utilized to prove every reaction step of polymer syntheses and to evidence three-dimensional structures at high lateral resolution. By using different marker molecules as well as specific molecule ion fragments, the combination of these two methods enables to obtain the precise characterization and evaluation of the different polymeric systems.

We present our results on the implementation of new methods for precise surface analysis of polymers. Starting with the investigation of molecular layered systems prepared via electrografting of surfaces followed by successive thiol-yne or thiol-ene reactions, we show controlled functionalization on silicon as well as on highly oriented pyrrolytic graphit substrates. Finally the developed strategy will be transferred to real graphite electrodes. This is an important step to design and tailor the properties of artificial solid electrolyte interfaces (SEI) for lithium ion batteries.

From the characterization of these two dimensional systems (according to the surface analytical tasks), we follow up with polymer systems with three dimensional analysis questions. We present analytical results of network formation using the *Para*-fluoro-thiol reaction and strategies for the confirmation of polymer position after polymerization within defined geometries. Surface analytical recipes to confirm synthesis routes were established. The analytical results of the three dimensional chemical picture are taken to further optimize the synthesis routes and network properties.

We kindly acknowledge the SFB 1176, funded by the German Research Council (DFG), in the context of projects B2, C1, C4 and Z1 for funding. The K-Alpha+ instrument was financially supported by the Federal Ministry of Economics and Technology on the basis of a decision by the German Bundestag.

10:00am **AS+BI+MI-MoM6 Combining Monoatomic- and Cluster Ion Sputtering in ToF-SIMS and XPS Depth Profiling of Organic-inorganic Multilayer Structures**, ***Eric Langer***, *J.-P. Barnes, O.J. Renault, T. Maindron*, CEA-Leti, France, *L. Houssiau*, University of Namur, Belgium

Organic electronics have risen to great importance in the world of consumer electronics. Especially organic light emitting diode (OLED) displays have brought new possibilities to the market. However, organic materials are more susceptible to electrical dysfunctions than conventionally used inorganic materials. This leads to a shortened lifetime for those materials. Environmental impacts like humidity or ultraviolet irradiation can create chemical reactions that lead to dark spots and device failures. Additionally, the flow of current through the device can further promote device degradation and can even induce migration and diffusion of dopants and small molecules. Precise chemical depth profiling is therefore essential to identify sources of failure and improve the device lifetime of organic electronics. Surface analysis techniques such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) and x-ray photoelectron spectroscopy (XPS) are efficient tools to characterize the chemical composition in depth. With the recent introduction of gas cluster ion beam (GCIB) sources, it is possible to sputter through organic materials without inducing a significant amount of damage to the sample [1]. Typically, argon clusters (1000 – 5000 atoms per cluster) with low energy per atom ratios (1 – 5 eV/atom) are used for gentle sputtering. However, these low energies are not sufficient to break the atomic bonds in inorganic materials. This poses a major problem in the characterization of hybrid inorganic-organic devices.

In this work, we present an approach to overcome the difficulties in depth profiling of inorganic-organic interfaces. Green OLED devices are characterized by ToF-SIMS depth profiling using GCIB as well as monoatomic sources for sputtering. This allows for precise tracking of characteristic chemical species in both the inorganic and the organic parts of the multilayer structures. Additionally, XPS depth profiling is used to measure the sputter induced damage during analysis [2]. We show, that by optimizing the sputter parameters, the sputter induced damage can be minimized and precise and reliable chemical information of hybrid inorganic-organic devices can be gained by combining ToF-SIMS and XPS analysis.

This work was carried out on the Platform for Nanocharacterization (PFNC) at the CEA Grenoble.

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10:40am **AS+BI+MI-MoM8 Ultra High Surface Sensitivity – Elemental Analysis of the Outer Layer**, ***Thomas Grehl***, *P. Brüner*, *H.H. Brongersma*, ION-TOF GmbH, Germany

In materials science and applications, the outer surface plays a vital role for a range of properties and in general for the interaction of a solid with its surroundings. The chemical properties of the surface govern macroscopic properties like wettability/contact angle, but also the chemical interactions as in catalysis, corrosion or thin film growth. The outer surface and its understanding is crucial for catalysis, fuel cells, thin film formation, nanoparticles and a wide range of other processes.

The analysis of the outer surface is frequently hampered by the fact that the origin of the signal is not completely limited to the first atomic layer, but bulk and surface signals are mixed. This issue is avoided in the case of Low Energy Ion Scattering (LEIS). The elemental composition of the outer atomic layer is determined quantitatively and separately from deeper layers. We will demonstrate a number of cases where this is essential to draw the relevant conclusions and reveal surface properties that would not be detected by other surface analytical techniques.

Nevertheless, the combination of complementary techniques is always required to address complex problems. We will demonstrate how the combination of LEIS with other established analytical techniques is beneficial for a comprehensive analysis.

One of these cases is the interaction of Ar cluster ions with a solid sample: it is well known that the sputtering yield of massive argon clusters is some orders of magnitude larger for organic than for inorganic materials. Therefore, Ar cluster beams have been discussed as a means of removing atmospheric adsorbents from surfaces prior to analysis. Using thin film samples, we have evaluated this approach applying LEIS in order to detect the removal of the organic material and the influence on the underlying inorganic surface. Despite the low sputtering yield for the inorganic material, a complete removal of the organic material will lead to a significant modification of the inorganic surface even when the actual erosion is limited.

Other examples from nanoparticles, catalysis and thin films will support the importance of outer layer surface analysis for materials research and other applications.

11:00am **AS+BI+MI-MoM9 Towards Predictive Understanding of Li-S Battery Materials through Multimodal Analysis**, ***Vijayakumar Murugesan***, *K. Han*, *M.I. Nandasiri*, *V. Shutthanandan*, *S. Thevuthasan*, *K.T. Mueller*, Pacific Northwest National Laboratory

Comprehensive understanding about the interfacial reactions between electrode and electrolyte is the major knowledge gap which inhibit the development of the lithium sulfur (Li-S) batteries. Despite numerous studies, the interfacial reaction mechanism such as SEI layer evolution and polysulfides dissolution process is still unclear. Hence, it is critical to develop a multi-modal approach that can provide unprecedented chemical imaging of complex interfaces in wide lateral (ranging from subatomic to micron) and temporal scales (few ns to seconds). Herein, we report an *in-situ* X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and nuclear magnetic resonance (NMR) combined with ab initio molecular dynamics (AIMD) computational modelling to gain fundamental understanding about the complex interfacial interactions in Li-S batteries. A multi-modal approach involving AIMD modelling and in situ XPS and NMR characterization uniquely reveals the chemical identity and distribution of active participants of interfacial reactions as well as the -battery capacity fading mechanism.

11:20am **AS+BI+MI-MoM10 Combined use of Back Side SIMS and FIB Sample Preparation**, ***Mikhail Klimov***, University of Central Florida

When profiling multilayered samples or even a homogeneous samples with rough surface SIMS depth resolution can suffer a rapid deterioration, particularly when polycrystalline metal layers are concerned. The back side SIMS was traditionally used to alleviate a loss of depth resolution during front side depth profiling. The traditional back side SIMS sample preparation involves painstaking polishing or/and ion milling, that requires considerable skills to produce a high quality finish surface that is parallel to front surface and terminated not too far from the interface of interest. Also, because the traditionally prepared sample is relatively large, the precise site specificity is, in general, unattainable.

I offer a relatively expedient FIB sample preparation (~2hrs.) for back side SIMS analysis at precise location and at exact distance from the front surface. The FIB sample extracted from the bulk has a typical lateral dimensions of 10 μ by 10 μ or less. In order to analyze such a small area, even smaller ion beam is required with diameter of 1μ or less to provide good depth resolution and high sensitivity. Also, it's very much desirable that the ion beam was Oxygen or Cesium to achieve a secondary ion yield enhancement, particularly important for small area analysis. In my case, micron and sub-micron beam of O_2^+ ions was produced by RF Plasma source by Oregon Physics that replaced, for the first time, Duoplasmatron on ADEPT1010 Dynamic SIMS System by Physical Electronics.

The FIB sample preparation procedure is discussed in detail and the first back side SIMS results compared to the front side depth profiles.

11:40am **AS+BI+MI-MoM11 Phase Quantification of Mixed TiO_2 Powders by X-ray Photoemission Valence Band Analysis and Raman Spectroscopy**, ***Paul Mack***, *T.S. Nunney*, Thermo Fisher Scientific, UK, *R.G. Palgrave*, University College London, United Kingdom of Great Britain and Northern Ireland

Titanium dioxide is one of the most studied materials in surface science. It has applications in heterogeneous catalysis, dye-sensitised solar cells, bone implants and self-cleaning windows. Many polymorphs of TiO_2 are known to exist but only two occur naturally in abundance: rutile and anatase. Rutile is the more thermodynamically stable form but anatase is more energetically favourable when forming nanoparticles at atmospheric temperature and pressure. The anatase polymorph has been recognised as more photoactive than rutile, although recent research indicates that the greatest photovoltaic efficiencies are achieved in devices that contain a mixture of anatase and rutile. The degree of mixing between two polymorphs influences other material properties, such as catalytic activity. This raises the question: how can one determine the polymorph ratio in a sample that contains a mixture of anatase and rutile?

Quantitative phase analysis of anatase-rutile mixtures by two experimental methods is presented in this work. Spectra of pure reference anatase and rutile were acquired X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy. These spectral shapes were then used to fit similar data from mixed phase samples. XPS and Raman spectroscopy give information from different depth regions in a sample. The surface sensitive character of XPS yields a surface phase fraction of anatase and rutile. Mixed phase samples were prepared from high and low surface area anatase and rutile powders. In this work, the surface phase fraction of anatase was found to be linearly correlated with photocatalytic activity of the mixed phase samples, even for samples with very different anatase and rutile surface areas.

Electronic Materials and Photonics Division
Room: 14 - Session EM+MI+TF-MoM

Growth, Electronic, and Magnetic Properties of Heusler Compounds
Moderators: Rehan Kapadia, University of Southern California, Seth King, University of Wisconsin - La Crosse

8:20am **EM+MI+TF-MoM1 Semiconducting Half-Heusler Heterostructures Grown by Molecular Beam Epitaxy**, ***Anthony Rice***, *S.D. Harrington, D.J. Pennachio, M. Pendharkar, C.J. Palmstrøm*, University of California at Santa Barbara

Half-Heusler (hH) compounds are an attractive family of materials for a number of applications due to their wide range of properties, including half-metallic ferromagnetism and topologically non-trivial surface states. Additionally, those containing 18 valence electrons per formula unit are predicted to show a semiconducting band gap [1]. This suggests the possibility of a single multifunctional material composed of compounds with the same crystal structure throughout which makes use of the diverse hH properties not accessible by traditional III-V technology as well as more traditional band gap engineering.

In this presentation, the heterointerface formed between the 18 valence electron semiconducting hHs, CoTiSb and NiTiSn, is investigated. Layered structures with both NiTiSn and CoTiSb, have been successfully grown on MgO(001) substrates using molecular beam epitaxy. Transmission electron microscopy and X-ray diffraction (XRD) data suggest separate layers with sharp interfaces. X-ray photoelectron spectroscopy (XPS) data shows no evidence of intermixing, with component peaks attenuating as expected. XPS is used to measure the valence band offset, which suggests a type-I heterojunction.

Through the use of CoTiSb buffer layers, the integration of NiTSn with III-V substrates is demonstrated. Previous attempts at direct growth of NiTiSn on III-Vs has proven unsuccessful due to the high reactivity of nickel with III-Vs. Reflection high-energy electron diffraction intensity oscillations during growth are observed for these structures, consistent with layer-by-layer growth. XRD interference fringes suggest abrupt interfaces. Higher quality NiTiSn is ultimately achieved, with lower carrier concentrations and higher mobility. Interface transport, both laterally and vertically, is also explored.

This work was supported in part by the Vannevar Bush Faculty Fellowship (ONR-N0014-15-1-2845) and NSF-MRSEC (DMR-1121053). The UCSB MRL Shared Experimental Facilities are supported by the MRSEC Program of the NSF under Award No. DMR 1121053; a member of the NSF-funded Materials Research Facilities Network. A part of this work was performed in the UCSB Nanofabrication Facility which is a part of the NSF funded National Nanotechnology Infrastructure Network.

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8:40am **EM+MI+TF-MoM2 Towards Topotronics: Combining Chemical Potential Tuning and Strain Engineering to Realize Surface Dominated Transport in Topological Heusler Thin Films**, ***Shouvik Chatterjee***, *J.A. Logan, N.S. Wilson, M. Pendharkar, C.J. Palmstrøm*, University of California at Santa Barbara

Heusler compounds have emerged as an exciting material system where realization of functional and tunable novel topological phases might be possible[1-4]. PtLuSb is one such compound that has been shown to host topologically non-trivial surface states[5]. However, being a semi-metal without a bulk band gap, exotic transport and thermodynamic properties expected from topological surface states are obscured by contributions from trivial bulk carriers that limits possible device applications[6]. Furthermore, natural defects in the compound leads to unintentional p-type doping resulting in the surface Dirac point lying above the chemical potential[5,6,7].

In this talk, I will present our efforts to address both these issues by a combination of carrier doping and substrate induced bi-axial strain to shift the chemical potential and attempt to open up a bulk gap, respectively. I will show experimental evidence of chemical potential tuning in Au alloyed $Pt_{1-x}Au_xLuSb$ thin films where the surface Dirac point can be pushed below the Fermi level. In addition, it is possible to open a bulk-band gap by application of compressive bi-axial strain on thin films synthesized on lattice mismatched substrates. Realization of surface dominated transport in topological Heusler thin films will open up avenues for realization of many exotic phenomena such as quantum anomalous Hall effect[8], axion insulators[9], topological superconductivity[10] and their potential device applications.

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9:00am **EM+MI+TF-MoM3 Topology, Magnetism, and Superconductivity in Ternary Half-Heusler Semimetals**, ***Johnpierre Paglione***, University of Maryland, College Park **INVITED**

In materials with non-centrosymmetric crystallographic structures, it has long been known that the lack of inversion symmetry can give rise to odd-parity spin-triplet pairing states. We report superconductivity and magnetism in a new family of topological semimetals, the ternary half Heusler compounds RPtBi and RPdBi (R : rare earth). In this series, tuning of the rare earth f-electron component allows for simultaneous control of both lattice density via lanthanide contraction, as well as the strength of magnetic interaction via de Gennes scaling, allowing for a unique tuning of both the normal state band inversion strength, superconducting pairing and magnetically ordered ground states. Antiferromagnetism with ordering vector (0.5,0.5,0.5) occurs below a Néel temperature that scales with de Gennes factor, while a superconducting transition is simultaneously linearly suppressed. With superconductivity appearing in a system with non-centrosymmetric crystallographic symmetry as well as p-orbital derived spin-3/2 quasiparticles, the possibility of high-spin Cooper pairing (i.e. beyond triplet) with non-trivial topology analogous to that predicted for the normal state electronic structure provides a unique and rich opportunity to realize both predicted and new exotic excitations in topological materials.

9:40am **EM+MI+TF-MoM5 Electron Counting, Surface Reconstructions, and Electronic Structure of 18 Electron Half Heuslers**, ***Jason Kawasaki***, University of Wisconsin - Madison, *A. Janotti*, University of Delaware, *C.J. Palmstrøm*, University of California at Santa Barbara

Half Heusler compounds (composition *ABC*) show great promise for the development of earth abundant thermoelectrics, half metallic ferromagnets for spin injection, and topological heterostructures. In these applications, the electronic structure of surfaces and interfaces are critical to materials performance. However, little is known about how and why the surfaces of these materials reconstruct or their direct effect on electronic properties. Using a combination of molecular beam epitaxy, angle resolved and core level photoemission, scanning tunneling microscopy, and density functional theory (DFT), we investigate the stability, reconstructions, and electronic surface states on the (001) surfaces of CoTiSb, NiTiSn, and FeVSb. These compounds are representative of a large class of 18 valence electron Half Heuslers that are expected to be semiconducting. We find that reconstructions in these compounds are characterized by *C* site (group IV or V) dimerization, as in III-V semiconductors, and this dimerization coincides with *B* site vacancies at the surface. We explain these trends using a simple electron counting model, and predictions from the model are in good agreement with both the experimental data and with DFT calculations. Our combined theoretical and experimental studies provide a rationale for understanding and controlling reconstructions and resultant electronic surface states in Heuslers.

10:00am **EM+MI+TF-MoM6 Computational Investigation of Heusler Compoundss for Spintronic Applications**, ***Jianhua Ma***, University of Virginia, *W.H. Butler*, University of Alabama

We present first-principles density functional calculations of the electronic structure, magnetism, and structural stability of 378 *XYZ* half-Heusler, 405 X_2YZ inverse-Heusler, 576 X_2YZ full-Heusler compounds. We find that a “Slater-Pauling gap” in the density of states in at least one spin channel is a common feature in Heusler compounds. We find that the presence of such a gap at the Fermi energy in one or both spin channels contributes significantly to the stability of a Heusler compound. We calculate the formation energy of each compound and systematically investigate its stability against all other phases in the open quantum materials database (OQMD). We represent the thermodynamic phase stability of each compound as its distance from the convex hull of stable phases in the respective chemical space and show that the hull distance of a compound is a good measure of the likelihood of its experimental synthesis. We find low formation energies and mostly correspondingly low hull distances for compounds with X = Co, Rh, or Ni, Y = Ti or V, and Z = P, As, Sb, or Si in half-Heulser compounds. In the half-Heusler family, we identify 26 18-electron semiconductors, 45 half-metals, and 34 near half-metals with negative formation energy that follow the Slater-

Pauling rule of three electrons per atom. In the inverse-Heusler family, we identify 14 asymmetric 18-electron semiconductors, 50 half-metals, and 42 near half-metals with negative formation energy. In the full-Heusler family, we identify 8 24-electron semiconductors and 23 half-metals with negative formation energy. Our calculations predict several new, as-yet unknown, thermodynamically stable phases, which merit further experimental exploration—RuVAs, CoVGe, FeVAs in the half-Heusler structure, and NiScAs, RuVP, RhTiP in the orthorhombic MgSrSi-type structure. Further, two interesting zero-moment half-metals, CrMnAs and MnCrAs, are calculated to have negative formation energy. In addition, our calculations predict a number of hitherto unreported semiconducting (e.g., CoVSn and RhVGe), half-metallic (e.g., RhVSb), and near half-metallic (e.g., CoFeSb and CoVP) half-Heusler compounds to lie close to the respective convex hull of stable phases, and thus may be experimentally realized under suitable synthesis conditions, resulting in potential candidates for various semiconducting and spintronics applications.

11:00am **EM+MI+TF-MoM9 Growth, Electronic, and Magnetic Properties of Half-Heusler CoTi$_{1-x}$Fe$_x$Sb**, ***Sean Harrington***, *A.D. Rice, T. Brown-Heft, A.P. McFadden, M. Pendharkar,* University of California at Santa Barbara, *O. Mercan, L. Çolakerol Arslan,* Gebze Technical University, Turkey, *C.J. Palmstrøm*, University of California at Santa Barbara

Recent predictions suggest the semiconducting half-Heusler compound, CoTiSb, exhibits half-metallicity when substitutionally alloyed with Fe. However, to date, few studies have examined the growth of high-quality single crystal thin films of Fe-alloyed CoTiSb. Here, we report the epitaxial growth of the substitutionally alloyed half-Heusler series CoTi$_{1-x}$Fe$_x$Sb by molecular beam epitaxy and the influence of Fe on the structural, electronic, and magnetic properties. CoTi$_{1-x}$Fe$_x$Sb epitaxial films are grown on InAlAs grown on InP (001) substrates for concentrations $0 \leq x \leq 1$. The films are epitaxial and single crystalline, as measured by reflection high-energy electron diffraction and X-ray diffraction. For films with higher Fe content, a lower growth temperature is necessary to minimize interfacial reactions. Using *in-situ* X-ray photoemission spectroscopy, only small changes in the valence band spectra from pure CoTiSb are detected. For films with $x \geq 0.05$, ferromagnetism is observed in SQUID magnetometry with a Curie temperature >400K. The saturation magnetization of the series increases linearly with Fe content as 3.4 μ_B/Fe atom. In comparison, there is a much smaller magnetic moment when the Fe is substituted on the Co site (Co$_{1-x}$Fe$_x$TiSb) indicating a strong dependence of the magnetic moment with site occupancy. A cross over from both in-plane and out-of-plane magnetic moments to only in-plane occurs for higher concentrations of Fe. Ferromagnetic resonance indicates a transition from weak to strong interaction as Fe content is increased. Temperature dependent transport shows a gradual semiconductor to metal transition with thermally activated behavior for $x \leq 0.3$. Anomalous Hall effect and magneto resistance are investigated for the x=0.3 and x=0.5 films revealing large differences in the electronic scattering mechanisms and transport behavior depending on Fe content.

11:20am **EM+MI+TF-MoM10 High Spin-Polarization and Perpendicular Magnetic Anisotropy in Single-Crystal Full-Heusler Co$_2$MnAl/Fe$_2$MnAl Superlattice**, ***Tobias Brown-Heft***, *A.P. McFadden, J.A. Logan,* University of California at Santa Barbara, *C. Guillemard,* University of Lorraine, France, *P. Le Fevre, F. Bertran,* Synchrotron SOLEIL, France, *S. Andrieu,* University of Lorraine, France, *C.J. Palmstrøm*, University of California at Santa Barbara

Ferromagnetic contacts are used as a source of spin-polarized current in many spintronic devices. Desired properties for ferromagnetic contacts used in magnetic tunnel junctions and other next-generation memory elements are perpendicular magnetic anisotropy and 100% spin polarization at the Fermi level (half-metallicity). Heusler compounds are strong candidates for this purpose as many have been predicted and observed to be half-metals (e.g. Co$_2$MnSi), while others exhibit perpendicular magnetic anisotropy (e.g. Co$_2$FeAl/MgO(001)). However, until now both properties have not been observed by experiment in a single material. J. Azadani *et al* have predicted that perpendicular anisotropy can be combined with half-metallicity by growing atomic-period superlattices of two different Heusler compounds [1]. We have successfully grown a single-crystal superlattice formed by layers of Co$_2$MnAl and Fe$_2$MnAl with periodicity of one to three unit cells using molecular beam epitaxy. X-ray diffraction reciprocal space mapping reveals that the superlattice is compliant to the substrate to at least 20 nm film thickness, sustaining strains from -3.0% (tensile) on MgO(001) to +2.3% (compressive) on GaAs(001). The film strain is accommodated via tetragonal distortion of c/a = 0 .96 to 1.06, respectively. The tetragonal distortion on GaAs(001) contributes to perpendicular magnetic anisotropy, resulting in films exhibiting out-of-plane magnetic easy axes at temperatures below 200K. Films with aluminum content higher than nominal stoichiometry may also help to induce perpendicular magnetization by reducing saturation magnetization, thereby lowering thin-film shape anisotropy. Superlattice structure was verified using electron energy loss spectroscopy in TEM, which shows low interface diffusion of cobalt and iron and high elemental contrast between individual superlattice layers. S pin polarization of >90% near the Fermi level has been measured directly via spin-resolved photoemission spectroscopy. Spin-resolved photoemission spectra suggest that the termination layer near a tunnel barrier interface should be Co$_2$MnAl-like, and may benefit from further composition tuning. This work was supported in part by C-SPIN, one of the six centers of STARnet, a Semiconductor Research Corporation program, sponsored by MARCO and DARPA. We also acknowledge support from the Vannevar Bush Faculty Fellowship.

[1] J. G. Azadani *et al*. J. Appl. Phys. 119, 043904 (2016).

11:40am **EM+MI+TF-MoM11 Formation of the Epitaxial MgO/Full-Heusler Co$_2$MnSi Interface: Oxygen Migration and Elemental Segregation**, ***Anthony McFadden***, *T. Brown-Heft, N.S. Wilson, J.A. Logan, C.J. Palmstrøm*, University of California at Santa Barbara

Magnetic tunnel junctions (MTJs) are an increasingly important emerging technology for both magnetic random access memory (MRAM) and spintronics applications. MTJs utilizing CoFeB magnetic electrodes and MgO tunneling barriers have received considerable interest for use in MRAM as desirable properties including perpendicular magnetic anisotropy, high tunneling magnetoresistance ratio, and current induced switching have been demonstrated. While CoFeB/MgO based MTJs have demonstrated remarkable performance, devices utilizing ferromagnetic Heusler compounds have the potential to surpass CoFeB based technologies due to a much higher predicted spin polarization. In addition, many Heusler candidates have even been predicted to be half-metallic (100% spin polarized at the Fermi-level). Of all predicted half-metals, the full-Heusler Co$_2$MnSi has received considerable attention as it is quite stable (ΔH_F = -0.441 eV/atom), has a high Curie temperature (T_c=985K), and a large minority-spin energy gap (571 meV). While Heusler based MTJs have the potential to surpass current CoFeB based technology, the spin polarization of Heusler compounds has been shown to be sensitive to atomic ordering, adding an additional challenge to materials growth and integration.

In the present work, the formation of the MgO/Co$_2$MnSi(001) interface has been studied *in-situ* using X-ray photoelectron spectroscopy (XPS). Co$_2$MnSi layers were grown on Cr-buffered MgO(001) substrates by coevaporation of elemental sources in ultrahigh vacuum while MgO was grown on the Co$_2$MnSi layers using e-beam evaporation of stoichiometric source material. It was found that partial oxidation of the Co$_2$MnSi surface was unavoidable during e-beam evaporation of MgO with oxygen bonding preferentially to Mn and Si. Interestingly, oxidation draws Mn and Si to the surface, resulting in an MgO/Co$_2$MnSi interface with composition significantly different from the unoxidized Co$_2$MnSi surface. In addition, Mn and Si oxides at the MgO/Co$_2$MnSi interface were reduced following annealing in UHV with a corresponding migration of oxygen from the interface into the MgO. The results of XPS studies have been correlated with temperature dependent transport measurements of fully epitaxial CoFe/MgO/Co$_2$MnSi MTJs which were observed to be highly sensitive to post-growth annealing temperature.

Surface Science Division
Room: 25 - Session SS+AS+MI-MoM

Organic/Inorganic Surfaces and Interfaces
Moderators: Liney Arnadottir, Oregon State University, Bruce Koel, Princeton University

8:20am **SS+AS+MI-MoM1 The Use of EC-STM to Study the Nanoscale Structure and Behavior of Atomically Thin Ag Films on Au Surfaces**, *J.A. Phillips, H.R. Morgan, L.E. Jackson, G. LeBlanc,* ***Erin Iski***, University of Tulsa **INVITED**

The formation of an atomically thin Ag monolayer on a Au(111) surface has been shown to significantly alter the 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 systems. EC-STM is a unique technique in that in addition to providing a local probe of the atomic surface structure, EC-STM 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. In addition to the ability to perform two kinds of Ag Underpotential Deposition (UPD) on Au(111) using a single solvent system (AgCl), this investigation also includes the examination of the effect of different halides on the thermal stability of the as-formed Ag monolayers. While it has been previously demonstrated that deposition from a AgCl system affords oxidative and thermal stability up to 1,000 K (1), the role of the identity of the halide has yet to be explored, specifically comparing depositions from both AgBr and AgI solutions. Preliminary investigations indicate that a monolayer formed from the AgBr system remains on the surface after the 1,000 K thermal treatment, while the same is not true for the AgI system. The origin of these differences will be examined in detail with EC-STM, CVs, and Density Functional Theory (DFT). Studies of this nature are critical to understanding the fundamental mechanisms behind thin film growth using UPD and the exact role of halides in the observed thermal stabilization. The ability to experimentally choose different surface properties based on electrochemical parameters and solution composition during deposition could lead to exciting new directions for thin film technologies.

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9:00am **SS+AS+MI-MoM3 Decomposition and Self-Assembly of Coronene on Pt(111)**, ***Chen Wang***, University of California Irvine, *K. Thurmer, N. Bartelt*, Sandia National Laboratories

Composed of seven benzene rings that form a larger, hexagonal structure, coronene is a molecule often referred to as “the smallest flake of graphene”. As such, this molecule provides insight into the nature and dominance of edge effects in graphene-based systems and devices. Furthermore, as a polynuclear aromatic hydrocarbon, coronene serves as a common chemical precursor and building block in soot formation, a process that is still largely mysterious in its earliest stages. This work presents the study of coronene assembly on Pt(111) at the nanoscale by using scanning tunneling microscopy and density functional theory calculations. Both experimental and theoretical methods focus on understanding the intramolecular interactions between neighboring molecules of coronene and with the underlying metal substrate by characterizing the molecular assembly at the monolayer and bilayer. At the monolayer, the platinum surface is highly interactive with the coronene, resulting in fragmentation of the molecule on and a high binding energy to the platinum surface. At the bilayer, platinum interference is screened, and several coronene-based structures are observed. In situ annealing allows for the observation of molecular clustering as the surface dewets. The coronene molecules first form chains, then clumps, and finally large clusters which bear notable resemblance to incipient soot. These findings are promising contributions to soot research and further general understanding of graphene at its the smallest scale.

9:20am **SS+AS+MI-MoM4 Understanding of Single-layer ZnS Supported on Au(111)**, ***Xingyi Deng***, *D.C. Sorescu, J. Lee*, National Energy Technology Laboratory

We investigate the structure and energetics of ZnS single-layer supported on Au(111) using a combination of experimental and theoretical approaches. Single-layer of ZnS, consisting of one atomic layer of ZnS(111) plane, has been grown on Au(111) via sulfurization of metallic Zn in H_2S at T = 550 K. ZnS single-layer on Au(111) forms a ZnS-(3 × 3)/Au(111)-(4 × 4) coincidence structure based on the LEED measurement. High resolution STM images reveal hexagonal unit cells of 6.7 × 6.7 Å^2 and 11.6 × 11.6 Å^2, corresponding to √3 and 3 times the unit cell of the ideal zincblende ZnS-(1 × 1), respectively, depending on the tunneling conditions. A significantly reconstructed non-planar structure of ZnS single-layer is suggested based on density functional theory (DFT) calculations. Specifically, 2/3 of the S anions are found to be located nearly in the plane of the Zn cations and the rest 1/3 of the S anions protruding above the Zn plane. These results are discussed and compared with other related systems, such as ultrathin ZnO supported on Au(111), in order to advance our understanding of materials in the ultrathin regime.

9:40am **SS+AS+MI-MoM5 X-ray Microscopy and Spectroscopy Insights of Metal-Organics Contacts**, ***Der-Hsin Wei***, *K.T. Lu, T.H. Chuang, C.I. Lu, Y.J. Hsu*, National Synchrotron Radiation Research Center, Taiwan, Republic of China

Abstract

After the giant magnetoresistance (GMR) was demonstrated in Co/Alq$_3$/LSMO trilayers [1], the rise of organic spintronics was no longer a question of if, but when. Latter it was even suggested that the interfaces are the most critical players toward the success of organic spinronics [2]. Unfortunately, despite much effort, vertical organic spin valve (OSV) could not establish a meaningful GMR at room temperature unless a thin insulator film is inserted between the ferromagnetic electrode and organic spacer [3-5]. Calls for spectroscopic studies were thus made to improve or even scrutinize the existing understandings [6]. In this report, I describe a jointed X-ray microscopy and spectroscopy investigations on multiple ferromagnet-organic hybrid structures including Co/pentacene, Fe/C$_{60}$, Co/C$_{60}$, and Ni/C$_{60}$. Our study indicates that the ferromagnetic (FM) 3*d* transition metals land on organic semiconductor (OSC) films suffer an apparent magnetization retardation. Further investigation reveals that there is more than a reactive interface behind the scenes. Finally, the connection between our findings and reported transport measurements is addressed.

Acknowledgments

Financial supports from Minister of Science and Technology (MoST) and National Synchrotron Radiation Research Center at Taiwan are greatly acknowledged.

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10:00am **SS+AS+MI-MoM6 Anchoring of Carboxylic and Phosphonic Acids on Atomically Defined Oxide Surfaces: The Role of Protons, Hydroxyl Groups and Water**, *M. Schwarz, T. Xu, S. Mohr, C. Schuschke*, ***Joerg Libuda***, University Erlangen-Nuernberg, Germany

Organic-oxide interfaces are at the heart of various emerging technologies, ranging from organic electronics to solar energy conversion. Their functionality arises from complex organic layers which are normally anchored to the oxide surface via specific linker groups. Typically, the anchoring groups release protons, thus forming surface hydroxyl groups. The role of these protons, the surface hydroxyl groups, and the interfacial water is one the most essential but, simultaneously, also one of the most poorly understood aspects in organic film formation.

We studied the interaction of water, carboxylic acids, and organic phosphonic acids with different cobalt oxide surfaces, namely Co_3O_4(111), CoO(111) and CoO(100), prepared in form of thin well-ordered films on Ir(100). The interaction of water with these surfaces is strongly structure-dependent and ranges from weak molecular adsorption on CoO(100) to the formation very strongly bound OH groups on Co_3O_4(111). Similarly, pronounced structure dependencies are observed upon anchoring of benzoic acid. Time-resolved and temperature-programmed vibrational spectroscopies with deuterated carboxylic acids indicate the formation of well-defined mixed adsorbate layers consisting of bridging benzoates and OD groups formed in the anchoring reaction. For phthalic acid, which may bind via one or via two linker groups, the adsorption geometry is controlled by the arrangement of the surface Co^{2+} ions. Organophosphonic acids, on the other hand, show a complex temperature-dependent anchoring behavior, which originates from the multiple adsorption geometries which these molecules can adopt. Finally, we investigated the anchoring behavior of larger organic species, such as carboxylated porphyrin derivatives, for which differently oriented phases can be observed by time-resolved in-situ spectroscopy during organic film growth in UHV. Intriguingly, the same reactions can also be monitored by in-situ vibrational spectroscopy at the solid/liquid interface on the same oxide surfaces prepared in UHV. We present first spectroscopic data, in which we directly compare these anchoring reactions in UHV and at the solid/liquid interface.

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10:40am **SS+AS+MI-MoM8 Thiolate *versus* Selenolate: Structure, Binding Strenght, Thermal Stability, and Charge Transfer Properties**, *J. Ossowski*, Jagiellonian University, Poland, *T. Wächter*, Universität Heidelberg, Germany, *T. Żaba,* Jagiellonian University, Poland, *L. Silies, M. Kind,* Universität Frankfurt, Germany, *A. Noworolska,* Jagiellonian University, Poland, *F. Blobner,* Technische Universität München, Germany, *D. Gnatek, J. Rysz,* Jagiellonian University, Poland, *M. Bolte,* Universität Frankfurt, Germany, *P. Feulner,* Technische Universität München, Germany, *A. Terfort,* Universität Frankfurt, Germany, *M. Zharnikov*, Universität Heidelberg, Germany, ***Piotr Cyganik***, Jagiellonian University, Poland

Selenolate is considered as an alternative to thiolate to serve as a headgroup mediating the formation of self-assembled monolayers (SAMs) on coinage metal substrates. There are however ongoing vivid discussions regarding the advantages and disadvantages of these anchor groups, regarding, in particular, the energetics of the headgroup-substrate interface, thermal stability and their efficiency in terms of charge transport/transfer. Here we introduce a well-defined model system of 6-cyanonaphthalene-2-thiolate and -selenolate SAMs on Au(111) to resolve these controversies. The exact structural arrangements in both types of SAMs are somewhat different, suggesting a better SAM building ability in the case of selenolates [1]. At the same time, both types of SAMs have similar packing densities and molecular orientations [1]. This permitted reliable competitive exchange and ion beam induced desorption experiments which provided an unequivocal evidence for a stronger bonding of selenolates to the substrate as compared to the thiolates [1]. The thermal analysis reveals higher stability of thiolates as compared to selenolates due to the higher stability of the S-C bond as compared to the Se-C which results from stronger bonding of selenolates with the Au(111) substrate [2]. Regardless of these differences, the dynamic charge transfer properties of the thiolate and selenolate based adsorbates were found to be identical as determined by the core-hole-clock approach, which is explained by a redistribution of electron density along the molecular framework, compensating the difference in the substrate-headgroup bond strength [1].

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11:00am **SS+AS+MI-MoM9 Preserving Material Morphology by Gas-Phase Functionalization: Surface Modification of ZnO with Propiolic Acid**, *F. Gao,* University of Delaware*, S. Aminane,* Université Pierre et Marie Curie, France*, S. Bai*, ***Andrew Teplyakov***, University of Delaware

Chemical functionalization of ZnO surface is commonly performed using reactions of carboxylic acids with the surface of this material. However, liquid phase reactions of carboxylic acids with ZnO often cause changes in surface morphology. Etching has been widely acknowledged as a potential problem in this functionalization process. This work will use gas-phase propiolic acid dosed in vacuum to modify ZnO nano-powder while preserving its morphology and leaving the alkyne group available for subsequent chemical modification via the azide–alkyne cycloaddition “click” reaction with benzyl azide. The formation of the surface carboxylate following gas-phase exposure of propiolic acid is shown to be a highly selective process confirmed by solid-state nuclear magnetic resonance spectroscopy, Fourier-transform infrared spectroscopy, and X-ray photoelectron spectroscopy. Electron microscopy is used to confirm that the morphology of the material is not affected during this modification and to compare with the liquid phase processing. It is also found that ZnO surface is stabilized by propiolic acid, as following this initial modification, further secondary postmodification based on either gas-phase exposure or liquid phase reactions were tested and confirmed to not affect the morphology of ZnO material. Based on this functionalization approach, delicate nanostructures, nanorods, or nanopowders and even ZnO-based devices can be chemically modified for further functionalization for applications where preserving surface morphology during chemical modification is especially important.

11:20am **SS+AS+MI-MoM10 Enhanced Long-range Magnetic Order by the Organic-Ferromagnetic Hybrid Interface**, ***Yao-Jane Hsu****, M.W. Lin*, National Synchrotron Radiation Research Center, Taiwan, Republic of China, *P.H. Chen,* National Tsing-Hua University, Taiwan, Republic of China, *Y.L. Lai,* National Synchrotron Radiation Research Center, Taiwan, Republic of China, *T.N. Lam,* National Chiao-Tung University, Taiwan, Republic of China, *D.H. Wei, H.J. Lin, Y.Y. Chin,* National Synchrotron Radiation Research Center, Taiwan, Republic of China*, J.H. Wang*, National Taiwan Normal University, Taiwan, Republic of China

The interplay between ferromagnetic and organic layers critically affects the efficiency of spin filtering in the organic/molecular spintronics. The hybridized properties at organic-ferromagnetic heterostructure is hence important. We investigated the spin interface in terms of the electronic structure and magnetic coupling of tetrafluorotetracyanoquinodimethane (F4-TCNQ) on nickel (Cu(100)/Ni) surface. The experimental results display magnetic hardening upon F4-TCNQ adsorbed on Ni surface. This enhanced magnetic ordering after molecular tailoring was studied by the surface-sensitive and element specific X-ray Magnetic Circular Dichroism (XMCD). The XMCD reveals that the orbital and spin moment of Ni is significantly increased on the in-plane, while that keep almost unaltered at out-of-plane. Through the strong superexchange coupling at in-plane surface, the nonmagnetic F4-TCNQ is spin polarized. Additionally, we found the enhanced magnetic ordering expressed larger domain sizes and less domain boundary from the measurements of surface magnetic anisotropy performed by magneto-optical Kerr effect (MOKE) and the magnetic domains inspected by photoelectron-emission microscope (PEEM). It suggests that the enhanced long-range magnetic order of organic-ferromagnetic interface is an effective spin filtering for constructing high efficient organic spintronics.

11:40am **SS+AS+MI-MoM11 Interaction of Coronene with Mo-C_{60} Nanospheres: The Effects of Substrate Curvature on Molecular Adsorption***,* ***Nathaniel W. Kabat****, E. Monazami, P. Reinke*, University of Virginia

Surface curvature has been observed to effect molecular adsorption, but little systematic work has been done in the regime where substrate corrugation is the same magnitude as molecule size. Here we present a scanning tunneling microscopy/spectroscopy (STM/STS) study of the interaction between molybdenum-fullerene nanospheres and coronene molecules. The nanospheres template is formed by a solid-state reaction between Mo thin films and a fullerene layer which is triggered by an annealing step. The reaction between the fullerenes and molybdenum breaks the symmetry of a fullerene layer but retains a dense molecular packing of visibly distorted fullerene-like structures. The electronic structure and bandgap of the nanospheres can be adapted by annealing and is driven by substitutional metal atom incorporation in the C_{60}. The interaction of coronene molecules with a gold surface serves as a model system representing the limiting case of a flat metallic surface and indicates that the molecular height varies with annealing temperatures while still exhibiting long range order. We will present coronene adsorption on nanospheres from wide bandgaps (2 eV) to fully metallic surfaces and discuss the adsorption geometries of coronene. We do not observe long range order of coronene molecules on the nanospheres surface, indicating that the localized nanosphere curvature has a strong influence on the absorption geometry. These results provide the beginning steps of understanding the ways in which nanosphere-molecule interaction can be controlled by the localized surface curvature. We acknowledge the support from the National Science Foundation award CHE-1507986 by the Division of Chemistry (Macromolecular, Supramolecular and Nanochemistry).

2D Materials Focus Topic
Room: 15 - Session 2D+MI-MoA

Novel 2D Materials
Moderator: Kathleen McCreary, Naval Research Laboratory

2:00pm **2D+MI-MoA2 Computational Characterization of 2D Perovskite Oxides Nanosheets**, ***Yanfu Lu***, *S. Sinnott*, Pennsylvnia State University

The metal oxides known as perovskites are well-known for a variety useful properties, including piezoelectricity, ferroelectricity, and magnetism. The bulk form of these materials has been well-studied over the last few years with computational materials science methods to better understand their structure-property relationships. More recently, two-dimensional (2D) materials “beyond graphene” have attracted substantial attention because of the potential for electron confinement and engineering of the electronic structure. According to V. Gopalan & R. Engel-Herbert (*Nat. Mater, 2016*), there are 389 theoretical predicted perovskite bulk structures, ABO_3 , where over half of them have been synthesized. When the same structure is synthesized in 2D form, the stoichiometry becomes $A_nB_{n-1}O_{3n+1}$. To identify perovskite oxides that may be produced as free-standing nanosheets, different thickness and different crystal orientation respect to the normal surface will be considered. When density functional theory (DFT) calculations are performing to each possibility, the accurate formation energy, lattice parameter, ionic polarization, and electronic bandstructure will be obtained to reveal the new ferroelectric, magnetic, and other properties associated with the formation of 2D materials from normally three-dimensional perovskite materials. The work performed here will consist of high-throughput first principles calculations. The results will be added to a searchable on-line database of 2D materials and freely disseminated to the community.

2:20pm **2D+MI-MoA3 Electronic and Optoelectronic Physics in the van der Waals Heterojunctions**, ***Philip Kim***, Harvard University **INVITED**

Recent advances of van der Waals (vdW) materials and their heterostructures provide a new opportunity to realize atomically sharp interfaces in the ultimate quantum limit. We demonstrate the enhanced electronic optoelectronic performances in the vdW heterostructures, suggesting that these a few atom thick interfaces may provide a fundamental platform to realize novel physical phenomena, such as hydrodynamic charge flows, cross-Andreev reflection across the quantum Hall edges states, and interlayer exciton formation and manipulations.

3:00pm **2D+MI-MoA5 Discovery of over 1000 New Two-dimensional Materials, 487 One-dimensional Molecular Wires and 98 Naturally Occurring Heterostructures**, ***Gowoon Cheon***, *K.-A.N. Duerloo, A.D. Sendek, C. Porter, Y. Chen, E.J. Reed*, Stanford University

Layered materials held together by weak interactions including van der Waals forces, such as graphite, have attracted interest for both technological applications and fundamental physics. Only a few dozen two-dimensional van der Waals solids have been subject to considerable research focus, although there likely to be many more and which could have superior properties. In this work, we identify 1173 two-dimensional layered materials and 487 materials that consist of weakly bonded one-dimensional molecular chains out of 58097 inorganic materials in the Materials Project. This is an order of magnitude increase in the number of identified materials, with most materials not known as two- or one-dimensional materials. To achieve this, we developed a novel data mining algorithm that determines the dimensionality of weakly bonded components contained in bulk, 3D crystal structures based on atomic bond lengths. Data mining allows for screening of all materials in the database, including but not confined to materials belonging to known families of two- or one-dimensional materials. Moreover, we identify 98 weakly bonded heterostructures that exist as bulk materials, opening new possibilities for much-studied assembly of van der Waals heterostructures.

Data on the families of materials, band gaps and point groups for the materials identified in this work are presented. Point group and piezoelectricity in layered materials are also evaluated in single-layer forms. 325 of these materials are expected to have piezoelectric monolayers with a variety of forms of the piezoelectric tensor. This work significantly extends the scope of potential low-dimensional weakly bonded solids to be investigated.

4:00pm **2D+MI-MoA8 Anisotropic 2D Palladium Diselenide with High Mobility for Air-stable Electronics**, ***Akinola Oyedele***, University of Tennessee, *L. Liang, A.A. Puretzky, S. Yang, A. Strasser,* Oak Ridge National Laboratory, *C.M. Rouleau*, Oak Ridge National Laboratory, *B.G. Sumpter, D.B. Geohegan,* Oak Ridge National Laboratory, *K. Xiao*, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Two-dimensional crystals are emerging materials for the realization of nanoelectronic devices including transistors, photodetectors, and chemical sensors. These ultra-thin electronics require candidate systems with high carrier mobility, sizeable and tunable bandgaps, and air stability, which are important for high-speed, durable applications. We present a new candidate, palladium diselenide ($PdSe_2$), with a similar puckered structure to black phosphorus, into the growing family of 2D materials. $PdSe_2$ exhibits a strong layer-dependent bandgap variation from ~0.2 eV (bulk) to ~1.3 eV (monolayer), and an electron mobility as high as ~330 $cm^2V^{-1}s^{-1}$ for few-layer systems. Due to their low-symmetry, $PdSe_2$ exhibits very interesting anisotropic behavior and the strong interlayer interaction is revealed from the large thickness-dependent Raman peak shifts, agreeing with first-principles Raman simulations. Unlike, black phosphorus, $PdSe_2$ is air-stable, thus making it a promising candidate that will spark interest for 2D electronics.

Acknowledgement: This work was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility.

4:20pm **2D+MI-MoA9 Hexagonal Boron-Carbon-Nitrogen – A Two-dimensional Direct Band Gap Semiconductor**, ***Axel Enders***, University of Bayreuth, Germany, *S. Beniwal*, University of Nebraska - Lincoln, *J. Hooper*, Jagiellonian University, Poland, *DP. Miller,* SUNY Buffalo, *P.S. Costa,* University of Nebraska - Lincoln, *S.Y. Liu*, Boston College, *E.C.H. Sykes*, Tufts University, *E. Zurek*, SUNY Buffalo

Two-dimensional h-BCN, synthesized from the precursor molecule bis-BN cyclohexane on the (111) surfaces of Ir and Rh under ultrahigh vacuum, was investigated with a comprehensively suite of in-situ local probe microscopy and spectroscopy methods. The lattice structure of h-BCN is identical to that of graphene, with the graphenic sites occupied by atoms of boron, nitrogen and carbon. The film morphology exhibits a strain driven corrugation with a periodicity of 3.2 nm, reminiscent of published results for epitaxial graphene and h-BN. Due to differences in the epitaxial fit and interfacial interactions, this corrugation is more ordered on the Rh surface. Out of several candidate structures that are feasible by connecting the B2C2N2 rings of the precursor molecules, the most likely film structure was established through combined density functional theory and X-ray photoelectron spectroscopy that studies the chemical environment of the film’s atoms. Local tunneling spectroscopy shows an electronic band gap of h-BCN of 1.0 eV on Rh(111) and of 1.5 eV on Ir(111). On the basis of these measured gaps and the computationally predicted electronic band structure, especially a direct electronic band gap that is intermediate to those of the zero-band gap semiconductor graphene and the insulating h-BN, and the theoretical prediction that the band gap is dependent on the molecular tiling, it can be expected that the h-BCN layers are potentially exciting candidates for 2D electronic materials.

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Magnetic Interfaces and Nanostructures Division
Room: 11 - Session MI+BI+EM+SA-MoA

Role of Chirality in Spin Transport and Magnetism
Moderators: Greg Szulczewski, The University of Alabama, Hendrik Ohldag, SLAC National Accelerator Laboratory

1:40pm **MI+BI+EM+SA-MoA1 Spin Transport and Polarization in Chiral Molecules: Theory and Possible Applications**, ***Karen Michaeli***, Weizmann Institute of Science, Israel **INVITED**

The functionality of many biological systems depends on reliable electron transfer. Unlike artificial electric circuits, electron transport in nature is realized via insulating chiral (i.e., parity-symmetry breaking) molecules. Recent experiments have revealed that transport through such molecules strongly depends on the electron's spin relative to the propagation direction. In the talk I will introduce the mechanism behind this phenomenon, which has been dubbed chiral induced spin selectivity (CISS). The discovery of the

CISS effect has raised important questions about the role of spin in biological processes more generally, and suggests the possibility of a new class of organic-based nanoscale devices. I will discuss some of the key developments regarding spin selectivity; I will present new questions that arise from these results and offer ideas for their resolution.

2:20pm **MI+BI+EM+SA-MoA3 Enantio-sensitive Charge Transfer in Adsorbed Chiral Molecules Probed with X Ray Circular Dichroism**, *F.J. Luque*, Universidad Autónoma de Madrid, Spain, *I.A. Kowalik*, Polish Academy of Sciences, Poland, *M.Á. Niño*, IMDEA-Nanoscience, Spain, *D. Arvanitis*, Uppsala University, Sweden, ***Juan José de Miguel***, Universidad Autónoma de Madrid, Spain

Recent studies have shown how layers of purely organic, chiral molecules can induce the appearance of strong spin polarization in initially unpolarized electron currents. [1] Furthermore, spin-polarized photoemission experiments comparing adsorbed films of opposite enantiomers of the same chiral molecule have revealed that they can display different behavior, producing spin polarization along different directions in space instead of simply changing its sign. [2]

In this study enantio-pure ultrathin films of chiral 1,2-diphenyl-1,2-ethanediol (DPED) have been deposited on Cu(100) at 100 K and studied at the MAX-lab synchrotron in Lund, Sweden, using circularly polarized x ray absorption (XAS) at the carbon K edge. XAS excites element-specific core electrons to empty levels in the ground state thus probing the molecule's electronic configuration. The different features present in the absorption spectra have been identified and assigned to specific electronic transitions. The comparison of absorption spectra taken with photons of opposite helicity shows a surprisingly strong dichroism localized at transitions into empty molecular orbitals with π character. Theoretical modeling of the spectra reveals that this response is associated to the charge transferred between the Cu substrate and the adsorbed molecules. This charge is found to be polarized in orbital momentum, and the direction of the polarization is different for the two enantiomers studied: (R,R)–DPED and (S,S)–DPED. These findings indicate that chiral organic layers can play an important role in the emerging field of molecular orbitronics.

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2:40pm **MI+BI+EM+SA-MoA4 Evolving of Soliton Phase in Exfoliated 2D $Cr_{1/3}NbS_2$ Nanolayers**, *S. Tang*, Oak Ridge National Laboratory and Central South University, China, *J. Yi, R. Fishman, S. Okamoto, Q. Zou*, Oak Ridge National Laboratory, *D.G. Mandrus*, University of Tennessee, ***Zheng Gai***, Oak Ridge National Laboratory

Cr1/3NbS2 is an emergent quasi-2D material that has recently been attracting wide attentions. Cr1/3NbS2 has both chiral helimagnetic behavior and broken inversion symmetry of Cr atoms, the two necessary conditions for creating Dzyaloshinskii–Moriya interaction in skyrmion. Bulk studies show that a nonlinear periodic magnetic state called a soliton lattice exists in the material. By applying microexfoliation techniques, we successfully prepared thin layers of Cr1/3NbS2 with various thickness from single crystal. When the thickness of Cr1/3NbS2 layer falls into the range around the pitch of its helimagnetic state, kinks of field dependent magnetization start to evolve. The new phase is studied experimentally and theoretically. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

3:00pm **MI+BI+EM+SA-MoA5 Tailoring the Chirality of Domain Walls via Interface Modification**, ***Arantzazu Mascaraque***, *S. Ruiz-Gomez, M.A. Gonzalez Barrio, L. Perez*, Universidad Complutense de Madrid, Spain, *G. Chen, A.K. Schmid*, Lawrence Berkeley National Laboratory, *E.G. Michel*, Universidad Autonoma de Madrid, Spain

The possibility of manipulating magnetic domain walls (DWs) without the intervention of magnetic fields has interest for a wide variety of applications, such as spintronic devices [1]. Applying an electric current to a ferromagnet creates a force that drives the DWs in the direction of the electron motion, the so-called Spin Transfer Torque. However, this effect is weak and high current densities are needed. Recently, it has been discovered that spin accumulation at the edges of a current-carrying non-magnetic material due to the Spin Hall Effect (SHE), can exert a torque on the magnetization of a neighboring magnetic layer [2]. The torque induced by SHE depends on the chirality of the DW and, as most ferromagnetic materials lack a well-defined chirality, the device applications are limited. However, the presence of surfaces and interfaces removes the point-inversion symmetry, giving rise to an additional interaction, the Dzyaloshinskii–Moriya interaction (DMI) that lifts the left-right degeneracy through spin-orbit coupling [3].

In this work, we have modified the interface between the substrate and a non-chiral magnetic layer, in order to investigate in which way DW chirality can be induced and stabilized in the magnetic layer. The experiments were done using the SPLEEM instrument of the Lawrence Berkeley National Laboratory. This microscope can map independently and in real space the three magnetic components of the spin structures. The magnetic system was a (Ni/Co)n multilayer epitaxially grown on Cu(111). It is well known that magnetic films grown on Cu(111) do not exhibit homo-chiral DWs [4]. We have found that this behavior can be changed by modifying the interface. After introducing a thin metal layer (suitable to induce a high DMI) between the substrate and the magnetic layer, we have found relevant changes in the chirality of the DWs of the magnetic layer. Our results demonstrate that the buffer layer influences the spin texture, which evolves from non-chiral Bloch to homo-chiral Néel DWs.

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3:20pm **MI+BI+EM+SA-MoA6 Spin Transport in an Electron Conducting Polymer**, ***Greg Szulczewski***, *T. Sutch, M. Lockart, H. Chen, P. Rupar, M. Bowman*, The University of Alabama

We report results from an electron spin resonance (ESR) study to probe the spin-dynamics in the conducting polymer poly {[N, N9 -bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5 9 -(2,2 9 -bithiophene)} or P(NDI2OD-T2). Chemical reduction of the polymer was achieved by using cobaltacene, which introduces unpaired electrons into the polymer. Continuous wave ESR measurements were done on frozen solutions and thin films over the temperature range of 77 to 300 K. Narrow ESR peaks with broad tails were observed, suggesting strong one-dimensional anisotropic conduction. Electron nuclear double resonance spectroscopy was used to analyze the hyperfine coupling of the frozen solutions. The results indicate a proton hyperfine coupling of 1.5 MHz, which suggests the spins are delocalized over several monomer units. Electron spin echo envelope modulation spectroscopy was measured from 6 to 90 K to investigate the spatial distribution of nuclear spins in the environment of the unpaired electrons spins. The measurements show that spin relaxation increases rapidly when the temperature in increases from 6 to 90 K. A kinetic model that accounts for the spin-dynamics will be presented.

4:00pm **MI+BI+EM+SA-MoA8 Utilizing the Chiral induced Spin Selectivity Effect to Achieve Simple Spintronics Devices**, ***Yossi Paltiel***, The Hebrew University of Jerusalem, Israel **INVITED**

With the increasing demand for miniaturization, nano-structures are likely to become the primary components of future integrated circuits. Different approaches are being pursued towards achieving efficient electronics, among which are spin electronics devices (spintronics) [1]. In principle, the application of spintronics should result in reducing the power consumption of electronic devices.

A new, promising, effective approach for spintronics has emerged using spin selectivity in electron transport through chiral molecules, termed Chiral-Induced Spin Selectivity (CISS) [2]. Recently, by utilizing this effect we demonstrated a magnet-less magnetic memory [3,4]. Also we achieve local spin-based magnetization generated optically at ambient temperatures [5,6]. The locality is realized by selective adsorption of the organic molecules and the nano particles [7]. Lastly we have been able to show chiral proximity induced magnetization on the surface of ferromagnetic and superconducting materials. The magnetization is generated without driving current or optically exciting the system [8,9].

In the talk I will give a short introduction about spintronics and the CISS effect. Then I will present ways achieve simple spintronics devices utilizing the effect.

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4:40pm **MI+BI+EM+SA-MoA10 Magnetic Nano Platelets based Spin Memory Device Operating at Ambient Temperatures**, ***Guy Koplovitz***, The Hebrew University of Jerusalem, *Y. Paltiel*, The Hebrew University of Jerusalem, Israel

There is an increasing demand for realizing a simple Si based universal memory device working at ambient temperatures. In principle non-volatile magnetic memory could operate at low power consumption and high frequencies. However, in order to compete with existing memory technology, size reduction and simplification of the used material systems are essential. In our work we use the Chiral Induced Spin Selectivity (CISS) effect along with 30-50nm Ferro-Magnetic Nano Platelets (FMNPs) in order to realize a simple magnetic memory device. The vertical memory is Si compatible, easy to fabricate and in principle can be scaled down to a single nano particle size. Results show clear dual magnetization behavior with threefold enhancement between the one and zero states. The magnetization of the device is accompanied with large avalanche like noise that we ascribe to the redistribution of current densities due to spin accumulation inducing coupling effects between the different nano platelets.

5:00pm **MI+BI+EM+SA-MoA11 Magnetization Switching in Ferromagnets by Adsorbed Chiral Molecules without Current or External Magnetic Field**, ***Oren Ben Dor****, The Hebrew University of Jerusalem, Israel

Ferromagnets are commonly magnetized by either external magnetic fields or spin polarized currents. The manipulation of magnetization by spin-current occurs through the spin-transfer-torque effect, which is applied, for example, in modern magnetoresistive random access memory. However, the current density required for the spin-transfer torque is of the order of 1×10^{6} $A\cdot cm^{-2}$, or about 1×10^{25} $electrons\cdot sec^{-1}\cdot cm^{-2}$. This relatively high current density significantly affects the devices' structure and performance. Here, we present a new effect – that of magnetization switching of ferromagnetic thin layers that is induced solely by adsorption of chiral molecules. In this case, about 10^{13} electrons per cm^2 are sufficient to induce magnetization reversal. The direction of the magnetization depends on the handedness of the adsorbed chiral molecules. Local magnetization switching is achieved by adsorbing a chiral self-assembled molecular monolayer on a gold-coated ferromagnetic layer with perpendicular magnetic anisotropy. These results present a simple low power magnetization mechanism when operating at ambient conditions.

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* **Falicov Student Award Finalist**

Applied Surface Science Division
Room: 13 - Session AS+MI+SS-TuM

Quantitative Surface Analysis: Effective Quantitation Strategies

Moderators: Kateryna Artyushkova, University of New Mexico, Gregory L. Fisher, Physical Electronics

8:00am **AS+MI+SS-TuM1 Effective Attenuation Lengths for Different Quantitative Applications of XPS**, *A. Jablonski*, Institute of Physical Chemistry, Warsaw, Poland, ***Cedric Powell***, NIST

The effective attenuation length (EAL) is a convenient parameter for use in place of the inelastic mean free path (IMFP) to account for elastic scattering of signal photoelectrons in XPS. The most common EAL application is measuring the thicknesses of overlayer films on planar substrate from the attenuation of substrate photoelectrons in laboratory XPS systems. EALs for this purpose can be obtained from a NIST database [1] and from empirical predictive equations [2]. In addition, EALs can be defined for other quantitative applications of XPS with laboratory XPS systems: (i) determination of thicknesses of overlayer films on planar substrates from changes of intensities of overlayer photoelectrons [3]; (ii) quantitative determination of surface composition by XPS [4]; and (iii) determination of shell thicknesses of core-shell nanoparticles [5]. Finally, EALs have been determined for measuring thicknesses of overlayer films on planar substrate from the attenuation of substrate photoelectrons in XPS with linearly polarized X-rays with energies up to 10 keV [6]. These EALs will be compared to corresponding EALs for unpolarized X-rays [2,6]. The EAL is not a simple material parameter like the IMFP but depends on the defining equation for the particular application as well as on the experimental configuration.

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8:20am **AS+MI+SS-TuM2 Plumbing the Depths using the XPS Inelastic Background**, ***Alexander Shard***, *S.J. Spencer*, National Physical Laboratory, UK

A novel semi-empirical description of the intensity of inelastically scattered electrons in XPS is introduced. The functional form describes the background over the full energy range of an XPS survey spectrum and is not intended to be used as a background subtraction method. Therefore, it may be used even in the absence of elastic peaks in the spectrum. Samples of gold and silicon oxide coated with defined thicknesses of Irganox 1010 and a calibrated XPS spectrometer were used to generate reference data. These data were used to establish appropriately linked functions for substrate and overlayer background shapes as a function of overlayer thickness and the known relative intensities and energies of the pure materials. A common functional form could be found and appears to be of general utility, at least for organic overlayers. The description shows that the measurement of overlayer thicknesses well beyond the traditional XPS information depth is possible, for organic layers on gold this can be larger than 50 nm. In principle, the background shape of any substrate beneath an organic overlayer can be described and the thickness adjusted to match experimental data.

This description of XPS background shapes may be employed to rapidly confirm the chemistry and depth of substrate materials. Discrepancies with thicknesses established by traditional analyses of elastic peak intensities can be employed to measure defect densities in coatings. The use of background shape analysis should also be useful for measuring the overlayer thickness on topographic materials where traditional angle-resolved analysis is not appropriate. Furthermore, these descriptions should be useful for new developments in XPS, such as nanoparticle shell measurement, high energy XPS and near-ambient pressure XPS.

8:40am **AS+MI+SS-TuM3 Quantitative Organic Depth Profiling and 3D Imaging using Secondary Ion Mass Spectrometry**, ***Rasmus Havelund***, National Physical Laboratory, UK **INVITED**

The development of gas cluster ion beams has transformed the ability for depth profiling of organic materials using secondary ion mass spectrometry (SIMS). The technique now permits molecular information to be obtained with excellent depth resolution to depths of several µm. This type of analysis is highly valuable across a range of applications but quantitative analysis continues to be a major challenge.

Carefully prepared organic reference multi-layers have in a number of studies been used to measure gas cluster ion sputtering yields[1,2], depth resolutions[1,2], and, recently, the matrix effect in binary molecular mixtures[3]. These parameters are important in any attempt to achieve quantification. Here, the ability to accurately measure the thickness of organic layers and the depth of interfaces is evaluated using such organic reference multi-layers. The depth of interfaces is needed for materials or devices consisting of distinct layers of pure single materials where a measurement of the thicknesses of the layers provides, quantitatively, the amount of substance in the layers. In sputter depth profiling, the thickness of a layer will be reflected in the primary ion dose required to remove the layer, and in the integrated characteristic secondary ion signal intensity through that layer. A detailed analysis of the critical role of the matrix effect on these parameters is provided, and the prospects for measuring compositions in mixed materials are discussed based on results from three different sample systems. This provides useful information for the development of quantification strategies.

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9:20am **AS+MI+SS-TuM5 Coupling Effects on the Intensity and Background of the Cr 3*p* Photoemission Spectrum around the Cr 2*s* Threshold**, ***Alberto Herrera-Gomez***, CINVESTAV-Unidad Queretaro, Mexico, *D. Cabrera-German*, Universidad de Sonora, *F.-S. Aguirre-Tostado*, CIMAV-Monterrey, *A. Dutoi*, University of the Pacific, *M.-O. Vazquez-Lepe*, Universidad de Guadalajara, *P. Pianetta*, Stanford University, *D. Nordlund*, Stanford Synchrotron Radiation Lightsource, *O. Cortazar-Martínez*, *L. Gomez-Muñoz*, CINVESTAV-Unidad Queretaro, Mexico, *A. Torrea-Ochoa*, CINVESTAV-Unidad Queretaro

By describing the photoelectric phenomenon as the absorption of a photon by a core electron and its subsequent emission, it is possible to understand many of the features found in XPS data ... as long as the photon energy is far away from the threshold of deeper core levels. For these cases, “the independent particle approximation, which had been thought to be applicable to atomic photoionization cross sections well above threshold, is clearly not applicable.”[1,2] Even at energies away from deeper thresholds, quantification of the composition can be done only if we are also willing to employ empirical background subtraction methods such as the Shirley function to assess peak intensities. Through this method, employed in conjunction with others methods accounting for the background due to inelastic scattering (i.e., Tougaard background), it is possible to properly reproduce the experimental background [3] and assess the composition of surfaces. Of course, the intensity related to the background is ignored for composition calculations. Ignoring the background due to inelastic scattering is perfectly self-consistent because these electrons are effectively accounted by the Debye-Waller attenuation factor calculated from the inelastic mean free path. However, there is not any attenuation factor to account for the ignored Shirley electrons.

Through the study of the peak intensity of the Cr 3*p* peak with photon energies around the Cr 2*s* threshold, we found that these two issues, 1) channeling effects on the peak intensity and 2) the need to ignore the Shirley electrons for composition calculations, are, in fact, related. The behavior of the Cr 3*p* background strongly suggest coupling between the 3*p* and the valence states. These coupling most exist for a brief time after photon absorption, and the observed photoelectrons should actually come from one of these coupled states. That is, “describing the photoelectric phenomenon as the absorption of a photon by a core electron and its subsequent emission” is not the complete paradigm for photoemission.

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9:40am **AS+MI+SS-TuM6 Using Main Peak Intensities for XPS Quantitation: Strengths, Weaknesses, Issues**, ***B. Vincent Crist***, XPS International LLC, *C.R. Brundle*, C. R. Brundle and Associates

It is common, in the practical world, to use the most intense XPS peaks from survey spectra, in combination with instrument software RSF's, for atom percent quantitation. The advantage is obvious: time saved. Occasionally, peak overlaps force the use of a secondary peak plus a ratio of RSF's. The origin of that ratio is usually based on theoretical cross-sections, σ (1), corrected for transmission function, T, and escape depth, λ.

Using clean elemental surfaces the validity of using relative σ's for peaks in the spectrum was tested. Some large discrepancies were found. The same occurred for some crystal materials and bulk polymers. Two possible causes are errors in σ's, or variations in intensity losses to satellites, invalidating the use of main peak intensities plus σ values (σ includes intensity from all final states). σ values should be good to better than 10% error (1). Intensity losses can vary with core level, but there are examples here where this does not seem to be the problem.

Suppliers' RSF's come either from theoretical σ's (1), or from empirical standards (2) where only main peaks are included. Except for 1st row elements there are significant discrepancies (>30%) between the approaches. We discuss possible reasons and note:

(a) the suppliers' empirical standard based RSF's all seem to be derived from the data of Wagner, et al. (2). That Herculean study included results from other studies on a range of poorly characterized instruments and samples whose surface compositions might be suspect.

(b) The discrepancies cannot be explained by the lack of inclusion of satellite intensities for the standards approach, as any correction generally worsens agreement.

We conclude it is time for a reexamination of the standards approach with modern instruments and better controlled samples. It is now possible to theoretically estimate the fraction of total intensity lost to satellites (3) and so to establish what fraction of σ should be used when relying on main peak intensities.

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2 C. D. Wagner, et al, Surface Interface Analysis, 3, 211, (1981)

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11:00am **AS+MI+SS-TuM10 XPS Spin-Orbit Splitting; Multiplet Splitting; Shake-up Losses: Implications for Determining Covalent Interactions and for Quantitative Analysis**, ***C. Richard Brundle***, C.R Brundle & Associates, *P.S. Bagus*, University of North Texas

The "apparent" spin-orbit (S-O) splitting of metal cation core levels, observed by XPS for 3d transition metals, can vary with the ligand (anion) concerned, [1], even though true S-O splitting is an atomic property not depending on the atom's environment. However, multiplet splittings of the core-level XPS of 3d cations depend on 3d shell occupation [1-3], so variation in this can alter the apparent S-O splitting. Such variation should have a consequence on the relative positions of the no-loss S-O component peak positions (ie the XPS "apparent" S-O splitting), via the well-established Mann and Aberg Sum Rule. [4]. Here we establish the importance of a mechanism that also contributes to changes in the multiplet splitting, and so in the apparent S-O splitting. This mechanism is covalent mixing of metal cation and ligand orbitals (for example Ref [5]), which alters the exchange integrals between core and valence electrons.

For a closed 3d shell, eg Ti^{4+} there is no possibility of multiplet splitting, but an apparent discrepancy in the S-O component intensity ratio has been reported (1), and an explanation proposed involving different intensity losses to shake-up satellites from each component. Our calculations indicate identical intensity losses, however, and a reanalysis of the experimental data indicates that the correct intensity ratio can be recovered by simply including the lifetime broadening of the $2p_{1/2}$ component, which results in overlap between it and the $2p_{3/2}$ component.

We present theoretical evidence, bare cation and cluster calculations, which provide quantitative estimates of the importance of various mechanisms for the covalency and for changes in apparent S-O splitting. These calculations allow comparison of "apparent S-O splitting" to "true" S-O splitting, the latter defined as the difference of the relativistic orbital energies of the S-O split levels. Furthermore, they permit establishing the differing importance of covalency for different ligands, and thus a connection to the observation of differences in core-level XPS for different ligands [6]. These effects also have a consequence for quantitative analysis using the 2p and 3p cation XPS peaks, which will be discussed.

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2. R. P. Gupta and S. K. Sen, Phys. Rev. B , 71 (1974)

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11:20am **AS+MI+SS-TuM11 The Cu *2p* Photoemission Spectra from Mixed Oxidation States**, ***Jorge-Alejandro Torres-Ochoa***, CINVESTAV-Unidad Queretaro, Mexico, *D. Cabrera-German,* Universidad de Sonora, Mexico, *M. Bravo-Sanchez,* Instituto Potosino de Investigación Científica y Tecnológica A.C, Mexico, *A. Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

Some X-ray photoelectron spectra have complicated structures that makes the peak fitting procedure difficult, especially with transition metals. Recent studies have shown the need to fit both branches of the *2p* spectra such as in Fe [1] and Co [2] This proved that modeling both branches concurrently is necessary to avoid errors such as area underestimation. In this report, copper films were obtained by sublimation in ultra-high vacuum ($5.5x10^{-8}$ torr) on Si(100) substrates. Immediately after deposition, the films were characterized by X-ray photoelectron spectroscopy using a monochromatic Al Kα source (hv=1486.7 eV). To study the initial stages of oxidation, the films were heat treated in an ultra-high purity oxygen atmosphere at 200 °C from 1 to 10 min.

From the photoemission spectrum, it was possible to observe three coexisting copper species. Using the Active Background Method,[3] an accurate fit was achieved for Cu *2p*. Both chemical species, Cu^{1+} (932.5 eV) and Cu^{2+} (933.5 eV), together with their satellites (Cu^{1+}: 946.5 eV, Cu^{2+}: 941.1 eV, and Cu^{2+}; 943.9 eV) were clearly identified.[4] The fit required two extra peaks at 934.7 eV and 942.4 eV. There is evidence that these peaks correspond to Cu^{3+}.

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11:40am **AS+MI+SS-TuM12 Quantifying Valence Band Offsets at Metal\\(Hf,Zr)O_2 Interfaces for Ferroelectric Devices**, ***Michael Brumbach***, *S. Smith, M.D. Henry, J. Dickerson, D. Robinson Brown, J. Ihlefeld*, Sandia National Laboratories

The compatibility of HfO_2 deposition with current silicon microelectronic processing make it an appealing alternative to traditional ferroelectrics. A variety of applications, including Tunneling Electroresistance devices, can benefit from the switchable polarization of HfO_2-based thin films, first reported in 2011. In these devices the optimal band-alignment for electron transport is dependent on selection of top and bottom contact materials. In this work, the valence band offset of $(Hf,Zr)O_2$ with a number of metal contacts has been quantified by X-ray photoemission measurements. Coupled with experiment, simulations have been performed to identify the band offsets for successful device operation. Metal contacts investigated include Pt, Ni, Au, Al, Ta, and TaN. For some metal films there is the experimental consideration for the impact of air oxidation on the measured valence band offsets. In addition to characterizing films in a bottom-up approach, the metal layers were ion milled to thin the overlying metal and reveal the interfacial boundary. In such cases, the oxide was removed and valence band offset values were measured. The role of differential sputtering in mono-atomic and the application of gas cluster ion sputtering to alleviate differential sputtering will be discussed. Additional techniques including inverse photoemission, UV-photoemission, and Kelvin probe will be presented for further quantification of the valence band offsets.

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12:00pm **AS+MI+SS-TuM13 Quantitative Peak-Fitting Analysis of the Photoemission Spectra of Metallic Zinc and Zinc Oxide Films**, ***Dagoberto Cabrera-German***, Universidad de Sonora, Mexico, *G. Molar-Velazquez, G. Gómez-Sosa,* CINVESTAV-Unidad Queretaro, Mexico, *W. De la Cruz,* Universidad Nacional Autónoma de México, *A. Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico

The quantitative analysis of the X-ray photoelectron spectra of Zn and ZnO is a challenging task due to plasmon-loss features and small binding energy shifts that lead to inaccurate results on the assessment of the chemical state of mixed systems of metallic zinc and zinc oxide.[1] Additionally, the Zn 2*p* spectra hold a complex background that traditional background modeling methods are unable to reproduce accurately.

We have analyzed the Zn 2*p* and O 1*s* spectra of a metallic Zn film that has been subject to pressure and time controlled oxidations at high vacuum. Through the state-of-the-art peak-fitting methods[2–4] we have overcome the difficulties, as mentioned earlier, of performing a quantitative analysis of a metal and oxide system and we have also noted several interesting features of the Zn 2p spectrum.

We found that the assessed chemical composition for several oxygen exposures is $ZnO_{1.00\pm0.10}$, this suggests that the set of peak parameters employed to resolve the metallic and oxide photoemission signals, are accurate and can be applied in quantitative studies.

The main characteristic of the peak-fitting procedure is that close experimental data reproduction requires an individual assignment of Shirley backgrounds for each peak comprising the spectra. Therefore an accurate quantitative analysis can only be done employing the Shirley-Vegh-Salvi-Castle (SVSC) background under the active approach.[2–4]

Another feature is that the intensity of plasmon-peaks and their background are not accurately described by any existing energy loss (intrinsic and extrinsic) formalism. In fact, the modeling of their background trend requires the addition of an intense Shirley contribution, up to 10 times larger than the Shirley contribution of the main photoemission line. These are outstanding results that suggest that these plasmon-peaks are produced by a loss process that remains unaccounted.

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Magnetic Interfaces and Nanostructures Division
Room: 11 - Session MI+2D+AC+SA+SS-TuM

Novel Magnetic Order at Interfaces
Moderators: Axel Enders, University of Bayreuth, Germany, Valeria Lauter, Oak Ridge National Laboratory

8:20am **MI+2D+AC+SA+SS-TuM2 Transition from Spatial to Magnetic Confinement in Graphene Quantum Dots**, ***Fereshte Ghahari***, *D. Walkup, C. Gutierrez,* NIST; Maryland NanoCenter UMD, *J.R. Rodiguez-Nieva,* Harvard University, *K.G. Watanbe, T. Taniguchi,* National Institute for Materials Science, Japan, *L.S. Levitov,* MIT, *N.B. Zhitenev, J.A. Stroscio,* NIST

Recent progress in creating and probing graphene quantum dots has offered a new platform to investigate Klein tunneling related phenomena. The quasi-bound resonances in these circular resonators can be confined even further by the application of a perpendicular magnetic field where they condense into highly degenerate Landau levels. Here, we use scanning tunneling spectroscopy to visualize the transition from spatial to magnetic confinement in quantum dots created in graphene/boron nitride heterostructures. In high magnetic fields, electrons redistribute themselves due to coulomb interactions leading to compressible regions separated by incompressible strips.

8:40am **MI+2D+AC+SA+SS-TuM3 Chiral and Proximity Induced Magnetism in Magnetic Multilayers and 2D Heterostructures**, ***Hyunsoo Yang***, National University of Singapore, Singapore **INVITED**

Topologically non-trivial chiral spin textures are present in systems with a strong Dzyaloshinskii-Moriya interaction (DMI) with a spatial extent of only tens to a few hundred nanometers. Thin film heavy metal/ferromagnetic bi- and multilayers have emerged as an ideal candidate for the development of such devices due to their tunability through a variation of the constituent components and relative layer thicknesses. However, to date, no chiral spin textures have been observed in thick ferromagnetic multilayers in which the disperate magnetic layers are exchange coupled. Furthermore, previous observations required either the presence of an out-of-plane bias field or careful tuning of a geometric confining potential to stabilize the skyrmion structure. In this work, we have imaged the formation of room temperature Néel skyrmions in a symmetric Co/Pd multilayer with Lorentz transmission electron microscopy for the first time [1]. Importantly, the size of the observed skyrmions is significantly smaller than previously reported systems in which non-multilayer films are used. The formation and resolution of the internal spin structure of room temperature skyrmions without a stabilizing out-of-plane field in thick magnetic multilayers opens up a new set of tools and materials to study the physics and device applications associated with magnetic chiral ordering.

Due to the unique topology associated with their band structure, two-dimensional (2D) transition metal dichalcogenides (TMDs) such as WSe_2, MoS_2 and WTe_2 provide a unique platform to develop novel electronics using the spin-valley degree of freedom. The incorporation of the heavy metal in the TMD suggests strong intrinsic spin orbit interactions, and could further result in a chiral DMI. However, confirmation of the DMI in such films and its effects on the spin ordering in the overlaying magnetic layer is lacking. Further, it has recently been predicted that orbital hybridization at the TMD/FM interface may occur and result in generation of a non-negligible magnetic moment in the TMD layer. In the present study we explore the interface induced magnetism in TMD/FM films. Finally, we also explore the effects of DMI and generation of chiral spin textures that result from it by measuring the imbalance between left and right-handed domains within the ferromagnetic layer. As the polarized neutron scattering is strongly dependent on spin chirality, this method has been utilized to study chiral magnetism in multilayer structures with strong DMI.

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9:20am **MI+2D+AC+SA+SS-TuM5 Surface Magnetism Induced by Interstitial Defects in PbO**, ***Elvis Arguelles***, Osaka University, Japan, *S. Amino,* A.L.M.T. Corp, Japan, *H. Nakanishi, S. Aspera, H. Kasai,* National Institute of Technology, Akashi College, Japan, *W.A. Dino,* Osaka University, Japan

We investigated the possibility of employing the polycrystalline αPbO as a spintronics device by *first principles* calculations based on the density functional theory (DFT). In particular, we explored the effects of *3d* transition metal atom, Fe on the structural and electronic properties of the layered αPbO (001) surface. Since it has been proven that ferromagnetic signals in experiments are often detected in thin films[1] we used a 2x2, 3-layered surface slab model of αPbO with 20 Å of vacuum space to simulate this environment in this study. The impurity atoms are placed in between the surface and subsurface of the crystal. The results show that the interstitial Fe interstitial forms shorter bonds with the oxygen atoms located at the surface and second layers. Also, this impurity is found to induce magnetism in the host crystal with magnetic moment value of 2.25 μ_B, which is highly localised on the transition metal.

In the bonding process, the Fe's lower energy lying *d* states form overlaps with nearest neighbour oxygen atoms with non-bonding *d* states situated near or at the Fermi level and are spin split. These spin split orbitals induce spin polarisation of *p* impurity states of oxygen atoms in the subsurface. Moreover, the magnetic order is determined using the energy difference between the antiferromagnetic and ferromagnetic states. The energy difference is 0.068 eV, suggesting that Fe interstitial impurities induce ferromagnetism in αPbO [2]. In this workshop, the effects of charge carriers to the magnetic properties will be briefly discussed. Finally, the position of the Fermi level in the density of states (DOS) suggests that in the case of α-PbO with Fe interstitials where the minority non-bonding *d* states are partially filled, the Zener's ferromagnetic double exchange mechanism may be dominant and stabilizing the ferromagnetic state.

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9:40am **MI+2D+AC+SA+SS-TuM6 XMCD Quest for Magnetic Proximity Effect in Ferromagnetic Insulator/Non-Magnetic Metal Interfaces**, ***Andrei Rogalev***, *F. Wilhelm*, European Synchrotron Radiation Facility, France

The rise of spin current physics together with enormous technological advances to engineer layered structures with tailoredspin-orbit interactions have placed 4d and 5d transition metals at the heart of the emerging fields of spinorbitronics, magnonics and caloritronics. In this context, magnetic properties at the interfaces between a ferromagnetic materials and non magnetic metals with large spin-orbit coupling play a central role. Some of those heavy metals like Pt or Pd are known to exhibit so-called magnetic proximity effect, i.e. they acquire interfacial induced magnetic moments whenever they are in contact with 3d metallic ferromagnets. However, when they are grown on magnetic insulators, e.g. yttrium iron garnet (YIG), whether induced magnetic moments are indeed ubiquitous is still an open question as contradictory reports have been published. This is indeed the key question for correct interpretation of the spin Hall magnetoresistance or the newly discovered unidirectional magnetoresistance phenomena and, in more general,to understand mechanisms of pure spin currents generation. To answer this question and to unravel a possible role of magnetic proximity effects at ferromagnetic/non-magneticinterfaces, X-ray magnetic circular dichroism (XMCD) spectroscopy appears to be the method of choice due to its element selectivity and high sensitivity. In this talk,we present a thorough review of XMCD experiments aimed at detection of magnetic proximity effect in a variety of ferromagnetic insulator/non-magnetic metal interfaces.

11:40am **MI+2D+AC+SA+SS-TuM12 Depth-Dependent Measurement of Atomic Valence and Magnetization in $La_{0.7}Sr_{0.3}MnO_3$ Magnetic Thin Films**, ***Mikel Holcomb***, *R. Trappen, S. Kumari, N. Mottaghi, S. Yousefi Sarraf, C.-Y. Huang, G. Cabrera,* West Virginia University

Magnetic thin films often lose their magnetic order and even bulk materials can have significant deviations of the magnetic order and other properties near surfaces and interfaces. In strongly correlated oxides, there are many competing parameters affecting the material properties, complicating the understanding of these systems. We utilize a combined approach of bulk and surface sensitive techniques measuring many film thicknesses to back out layer-by-layer properties in $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films. Strong changes from the bulk are observed for surfaces and interfaces. We will compare these models with theoretical predictions. LSMO has been widely proposed for diverse applications such as tunnel junctions and solid oxide fuel cells. Experimental support is provided by NSF (DMR-1608656). Theoretical support is provided by DoE (DE- SC0016176).

12:00pm **MI+2D+AC+SA+SS-TuM13 Coherent Magnetization Rotation of FeGa/NiFe Multilayers via Strain-Inducing Electric Field**, ***Colin Rementer***, University of California at Los Angeles, *M.E. Jamer,* NIST, *A. Barra,* University of California at Los Angeles, *J. Borchers, A.J. Grutter, B.J. Kirby,* NIST, *G.P. Carman, J.P. Chang,* University of California at Los Angeles

The ability to reduce the size of antennae would enable a revolution in wearable electronics, extendable to implantable electronic devices. Antenna miniaturization could be enabled by multiferroic materials, which enable the efficient control of magnetic via electricity. Multiferroic antennae, composed of coupled ferromagnetic and piezoelectric phases, could reduce antenna size by up to five orders of magnitude. This requires a magnetic material that is low loss, has an easily rotatable magnetization and is able to convert magnetic field to strain via magnetostriction.

Galfenol ($Fe_{84}Ga_{16}$, or FeGa) is a promising magnetic material due to its large magnetostriction (>200 ppm), high piezomagnetic coefficient (3 ppm/Oe), and high stiffness (70 GPa), but has high loss in the GHz regime. Permalloy ($Ni_{81}Fe_{19}$ or NiFe) is a soft magnetic material that has very low loss in the GHz regime (<20 Oe) but almost no magnetostriction. In this work, multilayer laminates containing alternating FeGa/NiFe layers were fabricated to reduce loss at high frequencies and properties were tuned via layer number and thickness. In this work, optimized multilayer laminates containing alternating FeGa/NiFe layers were shown to exhibit desirable magnetic softness (<20 Oe), narrow FMR line width (<40 Oe), high permeability (>400), and strong magnetostriction (> 70 microstrain). The focus of this work is to determine if the rotation of the magnetization of the individual layers is coherent with applied strain.

Polarized neutron reflectometry was used to determine the depth profiles of the structure and in-plane vector magnetization as functions of applied magnetic field and voltage. Initial studies showed that a FeGa/NiFe superlattice with the structure (20 nm FeGa/7 nm NiFe)/20 nm FeGa demonstrated coherent and linear rotation of magnetization with applied strain. To probe the thickness dependence of this rotation, three single NiFe/FeGa bilayers were fabricated on PMN-PT [011] with 40 nm, 20 nm and 7 nm of NiFe on a base layer of 20 nm FeGa. Application of 400 V results in an enormous increase in spin-flip scattering, unambiguously demonstrating a substantial rotation of the magnetization perpendicular to the applied magnetic field direction for all samples measured. Micromagnetic and finite element simulations support the experimental results, showing coherent rotation of the magnetization with only small deviations with thicker NiFe layers. These measurements provide direct evidence of a voltage-induced rotation of the both the NiFe and FeGa magnetization as well as a means to separate the response of the magnetostrictive and non-magnetostrictive layer components.

Nanometer-scale Science and Technology Division
Room: 19 - Session NS+EM+MI+SS-TuM

Nanoscale Electronics and Magnetism

Moderators: Keith Brown, Boston University, Aubrey Hanbicki, Naval Research Laboratory

8:00am **NS+EM+MI+SS-TuM1 Nanometrology and Nanocharacterization in Nanoelectronics**, ***Alain C. Diebold***, SUNY Polytechnic Institute **INVITED**

As the so called technology node for integrated circuits moves below 10 nm, new transistor and interconnect materials as well as new device structures are moving from research into development. Pseudomorphic semiconductor films such as $Si_{1-x}Ge_x$ on Si are expected to transition to Ge/$Si_{1-x}Ge_x$/Si or to III-V epilayers. The current lithographic processing used to pattern FinFETS is based on the Quadruple Spacer Patterning process which can result in two values of pitch walking. This greatly complicates in-line metrology. The FinFET itself will likely be replaced by nanowire transistors having multiple vertically stacked nanowire channels. Another alternative is the nano-sheet transistor. Beyond these evolutionary changes, longer term devices based on 2D materials are being investigated. These include graphene, transition metal dichalcogenides, and topologically protected materials. This talk will cover the advanced measurements being used to address the challenges associated with these new materials and structures. The talk will cover measurement methods including high resolution X-ray diffraction (XRD), XRD reciprocal space mapping, Mueller Matrix spectroscopic ellipsometry base scatterometry, and advanced electron microscopy.

9:00am **NS+EM+MI+SS-TuM4 Measurement of Resistance Induced by a Single Potassium Atom on Chiral-Angle Known Nanotubes: Understanding the Impact of a Model Scatterer for Nanoscale Sensors**, ***Masahiro Ishigami***, University of Central Florida, *R. Tsuchikawa,* University of Utah, *D. Heligman,* Ohio State University, *B.T. Blue,* University of Central Florida, *Z.Y. Zhang,* Columbia University, *A. Ahmadi, E.R. Mucciolo,* University of Central Florida, *J. Hone,* Columbia University

Even atomic impurities are expected to impact device properties of carbon nanotubes. Such sensitivity makes them ultimately useful for sensor technologies. Rational design for nanotube-based sensors requires precise understanding of how impurities impact transport properties of nanotubes. Such impurity-induced carrier scattering is expected to be dependent on the chirality of nanotubes and the nature of scattering potentials imposed by impurities. Yet until our recent measurements, it has been impossible to measure the impact of impurities on resistance of carbon nanotubes with known chirality.

We have developed arrays of experimental techniques to control experiments down to atomic scale to measure the scattering strength of charged impurities on semiconducting single-walled carbon nanotubes with known chirality. The resistivity of nanotubes is measured as a function of the density of adsorbed potassium atoms, enabling the determination of the resistance added by an individual potassium atom. Holes are scattered 37 times more efficiently than electrons by an adsorbed potassium atom. The determined scattering strength is used to reveal the spatial extent and depth of the scattering potential for potassium, a model Coulomb adsorbate, paving way for rational design of nanotube-based sensors. Our results are published in Phys. Rev. B [**94**, 045408 (2016)].

9:20am **NS+EM+MI+SS-TuM5 Atomic Electronics for Quantum Computing**, ***Michelle Simmons***, University of New South Wales, Australia **INVITED**

Extremely long electron spin coherence times have recently been demonstrated in isotopically pure Si-28 [1] making silicon one of the most promising semiconductor materials for spin based quantum information. The two level spin state of single electrons bound to shallow phosphorus donors in silicon in particular provide well defined, reproducible qubits [2] and represent a promising system for a scalable quantum computer in silicon. An important challenge in these systems is the realisation of a two-qubit gate, where we can both position donors with respect to each other for controllable exchange coupling and with respect to charge sensors for individually addressing and reading out the spin state of each donor with high fidelity.

To date we have demonstrated using scanning tunneling microscope hydrogen lithography how we can precisely position individual P donors in Si [3] aligned with nanoscale precision to local control gates [4] and can initialize, manipulate, and read-out the spin states [5,6] with high fidelity. We now demonstrate how we can achieve record single-electron readout fidelity for each of two donor based dots of 99.8%, above the surface-code fault tolerant threshold. We show how by engineering the quantum dots to contain multiple donors we can achieve spin lifetimes up to 16 times longer than single donors. Finally we show how by optimising the interdonor separation and using asymmetric confinement potentials we can create controllable exchange coupling in these devices. With the recent demonstration of ultra-low noise in these all epitaxial devices [7] these results confirm the enormous potential of atomic-scale qubits in silicon.

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11:00am **NS+EM+MI+SS-TuM10 Electronically Abrupt Borophene/organic Lateral Heterostructures**, ***Xiaolong Liu****, *Z. Wei, I. Balla, A.J. Mannix*, Northwestern University, *N.P. Guisinger*, Argonne National Laboratory, *E. Luijten, M.C. Hersam*, Northwestern University

Two-dimensional (2D) boron, known as borophene, has recently been experimentally realized[1,2] following theoretical predictions.[3] As an elementary 2D material, borophene is determined to be metallic like graphene, but also possesses a high degree of in-plane anisotropy like phosphorene. Thus far, all experimental studies have been performed on borophene alone, whereas borophene-based electronic applications will require precise integration of borophene with other materials. Here, we demonstrate the self-assembly of a borophene/organic lateral heterostructure[4]. Upon the deposition of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on sub-monolayer borophene on Ag(111), the molecules preferentially self-assemble into monolayers on bare Ag(111), forming borophene/PTCDA lateral heterostructures spontaneously. This phenomenon is consistent with a lower adsorption energy of PTCDA molecules on borophene, as modeled via molecular dynamics simulations. The formation of the heterostructure leaves the chemical integrity of borophene unperturbed as supported by in situ X-ray photoelectron spectroscopy. In addition to structural properties, atomic-scale ultra-high vacuum scanning tunneling microscopy and spectroscopy reveal strong electronic contrast between the two materials and an electronically abrupt heterojunction with a transition distance of ~1 nm (i.e., approximately the size of one PTCDA molecule). Across this transition region, the differential tunneling conductance curves change from the metallic electronic structure of borophene to the semiconducting molecular orbitals of PTCDA, suggesting the formation of an atomically abrupt 2D metal-semiconductor junction. Overall, the results of this study are likely to inform future research on borophene functionalization for nanoelectronic applications.

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11:20am **NS+EM+MI+SS-TuM11 Mechanical Characterization of Heat Dissipation in a Current-driven Ferromagnetic Resonance System**, *S.U. Cho, M. Jo, S. Park, J.-H. Lee, C. Yang, S. Kang*, Seoul National University, ***Yun Daniel Park***, Seoul National University, Republic of Korea

Heat dissipation in current-driven ferromagnetic resonance (FMR) system is characterized by monitoring the mechanical resonance, which shifts are governed by thermoelastic properties. Realization of a free-standing Permalloy (Py)/Pt bilayer strip, with an added mechanical degree of freedom, advantageously integrates means to separately measure mechanical resonance, by piezoresistive transduction in Pt [1], and FMR by using the spin-torque FMR (ST-FMR) measurement technique [2]. Heat generated by the precessing magnetization under an electric driving current are selectively investigated by monitoring the mechanical resonance shift, which are immune and independent to thermoelectric effects. By comparing the angular dependence to the applied magnetic field direction of the two FMR spectroscopies, ST-FMR and mechanical heat reaction, we find that Joule heat resulting from a time-dependent magnetoresistance, which in turn arises from the precessing magnetization and electrical current, cannot be overlooked in addition to the intrinsic FMR heat dissipation.

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11:40am **NS+EM+MI+SS-TuM12 The Exciting Physics of Spin Chains Coupled to a Metallic Substrate**, ***Roland Wiesendanger***, University of Hamburg, Germany **INVITED**

A magnetic nanowire on the surface of a spin-orbit coupled s-wave superconductor is a fascinating platform, which has been proposed for observing the emergence of zero-energy Majorana bound states at the ends of the wires [1]. Majorana fermions can encode topological qubits and ultimately provide a new direction in topological quantum computation [2]. Most recently, evidences for topologically non-trivial end-states were experimentally found for self-assembled ferromagnetic Fe nanowires on superconducting Pb(110) substrates by using scanning tunneling microscopy and spectroscopy (STM/S) as well as non-contact atomic force microscopy methods [3-6]. However, self-assembled nanowires of Fe on Pb surfaces have unavoidable limitations, such as (1) intermixing of atomic species of the nanowire and the substrate during the annealing process, and (2) uncontrolled length and orientation of the nanowires.

Here, we demonstrate the fully-controlled bottom-up fabrication of artificial 1D atomic chains from individual magnetic Fe adatoms on high spin-orbit coupled non-superconducting Pt(111) and superconducting Re(0001) substrates by utilizing STM-based atom-manipulation techniques at T=350 mK. Spin-polarized STM measurements indicate the presence of non-collinear spin textures, i.e. spin spiral ground states, stabilized by interfacial Dzyaloshinskii-Moriya interactions similar to self-assembled Fe chains on Ir(001) investigated earlier [7]. The problem of intermixing is avoided by the low-temperature fabrication of the chain and an appropriate choice of the substrate, while single-atom manipulation allows the construction of chains with a given number of atoms and orientation. Tunneling spectra measured spatially resolved on the Fe-atom chain on Re(0001) reveal the evolution of the local density of states (LDOS) inside the superconducting gap as well as the development of zero-energy bound states at the ends of the chain, which are distinguishable from trivial end states by systematically increasing the number of atoms within the Fe-atom chain. The experimental results will be compared with model-type calculations supporting the interpretation of the spectroscopic signatures at the ends of the chains as Majorana bound states.

(work done together with Howon Kim and Khai Ton That).

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* **NSTD Student Award Finalist**

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room: 9 - Session SA+MI-TuM

Overcoming the Temporal and Spatial Limits of X-Ray Scattering Methods for In-Situ Analysis

Moderators: Olivier Renault, CEA/LETI-University Grenoble Alpes, France, Zahid Hussain, Advanced Light Source, Lawrence Berkeley National Laboratory, Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy

8:20am **SA+MI-TuM2 SA Highlight Talk: Diffraction Limited Storage Rings and Free Electron Lasers --- Why do we need both?**, ***Wolfgang Eberhardt***, DESY-CFEL, Germany

Accelerator driven photon sources have experienced a phenomenal development and success over the last decades. Worldwide many thousands of scientists travel to these facilities to conduct their research and new and upgraded facilities are under construction in several countries around the world. While storage ring based facilities have been at the heart of this effort until recently, the attention has somewhat turned to the construction of free electron laser facilities. As the pricetag for each of these facilities is in the range of 100's of million $, and even surpassing 1 B$, the question arises, whether science and society really needs both kind of facilities.

In this talk I will give examples of experiments that are unique to each of these light sources, emphasizing the need for both --- state of the art DLSR's and FEL's ---- to meet the challenges of future science and society.

8:40am **SA+MI-TuM3 Understanding Solar Cells Structure and Functioning via GISAXS and GIWAXS**, ***Peter Müller-Buschbaum***, Technische Universität München, Germany **INVITED**

Next generation solar cells are an interesting alternative to conventional silicon based solar cells as the feature new possibilities introduced by using a different class of materials namely polymers. The production of next generation solar cells has the potential to become very cheap and easy. Moreover, the use of polymers allows for flexible solar cells and light weight devices, which will be usable in a very different fashion as compared to the immobile silicon solar panels. In addition, the energy payback times of next generation solar cells are significantly shorter as compared to the today’s silicon solar cells. However, despite all these significant advantages of next generation solar cells, still fundamental knowledge is very limited.

In particular, it is challenging to detect the complex morphologies, which are necessary to have high efficiency organic solar cells. The combination of grazing incidence small and wide angle x-ray scattering (GISAXS and GIWAXS) allows for overcoming these challenges.[1-4] The crystalline structure is probed with GIWAXS and the mesoscale structure is determined with GISAXS. Based on selected examples, the impact of different layers in the functional stack build-up of organic solar cells,[5,6] in-situ studies during printing[7] and in-operando studies of organic solar cells[8] are presented.

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9:40am **SA+MI-TuM6 In situ Characterization of the Structure Formation in Printed Organic Thin Films for Photovoltaic Applications**, ***Stephan Pröller***, TU Munich, Germany, *F. Liu*, Shanghai Jiao Tong University, PR China, *C. Zhu*, Lawrence Berkeley National Laboratory (LBNL), *D. Moseguí González*, TU Munich, Germany, *C. Wang, E. Schaible, T.P. Russell, A. Hexemer*, Lawrence Berkeley National Laboratory (LBNL), *P. Müller-Buschbaum*, Technische Universität München, Germany, *E.M. Herzig*, University Bayreuth, Germany

The nanomorphology can strongly influence the physical properties of organic thin films. For example, polymer:fullerene blends used in organic solar cells vary significantly in performance depending on the inner film morphology. To allow large-scale production of these devices, control of the nanostructure during the processing of the active layer is important. This firstly needs an understanding of the processes involved during the drying of the film. In a second step we can then manipulate the drying processes to alter the nanostructure. Using an industrial slot-die coater implemented into a synchrotron beamline we have successfully characterized the solidification process of an active layer using grazing incidence small and wide angle X-ray scattering (GISAXS/GIWAXS). Tracking the actual crystallization and aggregation processes on length scales ranging from sub-nanometers to several tens of nanometers reveals how the different growth processes compete with each other leading to the final film morphology. To achieve this, we follow the evolution of the nanostructure with appropriate time-resolution to initially track the solvent removal, followed by the crystallization of the polymer and the aggregation of the fullerene. We find that the morphological evolution can be separated into several subsequent phases that take place independently of the drying speed of the film. The final film morphology, however, depends on the processing speed, because the individual processes compete with each other differently depending on time. Using an environmental control system, we are able to further control the solvent evaporation and hence the structure formation during processing.

S. Pröller, F. Liu, C. Zhu, C. Wang, T.P. Russell, A. Hexemer, P. Müller-Buschbaum, E.M. Herzig, Advanced Energy Materials, 6: 1501580 (2016)

11:00am **SA+MI-TuM10 Ultrafast X-ray Scattering Studies of Light-induced Processes in 2D Materials**, *A. Lindenberg*, ***Edbert Sie***, Stanford University **INVITED**

Novel characterization techniques developed over the past two decades have revolutionized our ability to visualize the microscopic, atomic-scale processes that determine the functional properties of materials. The overarching challenge here is that the relevant time-scales and length-scales for these processes are typically 10^{-13} seconds (100 femtoseconds) and 10^{-10} m (1 Å) such that our view of how a material functions is often blurred out in time or in space. In this talk I will describe recent experiments using femtosecond x-ray pulses as a means of probing and manipulating the optoelectronic and structural properties of materials on ultrafast time-scales, as they transform and *in-situ*. I will focus in particular on recent experiments probing dynamic deformations of multilayer transition metal dichalcogenide films on femtosecond and picosecond time-scales. These studies reveal a surprising light-induced nonlinear modulation in the interlayer bonding, associated with manipulation of the Casimir/van der Waals interaction between quasi-2D layers.

11:40am **SA+MI-TuM12 Monitoring the Non-Metal to Metal Transition and Ultrafast Charge Carrier Dynamics of Supported Clusters by Femtosecond XUV Photoemission Spectroscopy**, ***Mihai Vaida***, University of Central Florida, *M. Marsh, B. Lamoureux, S.R. Leone*, University of California at Berkeley

Understanding the electronic structure and charge carrier dynamics of supported clusters is extremely important due to their many potential applications in photochemistry and catalysis. Time resolution, surface sensitivity and element specificity are technical ingredients required to investigate ultrafast photoinduced processes of charge migration, localization and recombination at clusters on a solid surface. All these requirements are fulfilled by a new experimental technique based on pump-probe photoemission spectroscopy (PES) in conjunction with femtosecond extreme ultraviolet (XUV) laser pulses that will be presented in this contribution. The ultrafast electron and hole charge state dynamics is investigated by monitoring the ultrafast photoinduced transient charging of the clusters at surface by core level and Fermi level photoelectron spectroscopic shifts.

Gold clusters grown on 10 ML MgO(100)/Mo(100) are investigated as a model system for using static XUV photoemission as a probe of electronic character versus cluster size. As the size of the Au clusters is increased, a gradual shift in the photoemission onset up to the Fermi energy indicates a change in the character of the gold clusters from non-metallic to metallic. The results are compared with theoretical work and previous investigations to validate the XUV-PES method. Static photoemission is then further utilized to monitor the electronic structure of Zn clusters on p-Si(100) as a function of Zn deposition. The transition from non-metallic to metallic Zn character is observed at 0.16 ML of Zn coverage. Furthermore, the femtosecond pump-probe XUV-PES technique is employed to induce a charge transfer from the p-Si(100) substrate to the Zn clusters and to measure in real time the charge trapping at the Zn clusters as well as the subsequent charge relaxation. The ultrafast charge carrier dynamics investigations are performed as the Zn dimensionality is increased from small clusters composed of a very few atoms to large collections of atoms to extended Zn films.

12:00pm **SA+MI-TuM13 Direct Observation of TiO_2 Exciton Recombination**, ***Geoff Thornton***, Universty College London, UK, *Y. Zhang, D. Payne, C. Pang,* University College London, UK, *C. Cacho, R. Chapman, E. Springate,* STFC Rutherford Appleton Laboratory, UK

Exciton recombination pathways are of paramount importance in photocatalysis because they determine the lifetime of the chemically active electrons and holes, and hence the catalytic efficiency. These pathways are not known in detail even for a prototypical material such as TiO_2, where the related process of electron trapping is important in a broader range of applications (eg resistive switching). Here we use time-resolved femtosecond pump-probe photoemission spectroscopy (TRPES) to investigate exciton recombination and electron trapping in a state resolved fashion. This employed an XUV probe following an infra-red or UV pump. When an infra-red pump is employed, electrons in polaronic band gap states (BGS) are excited to the bottom of the conduction band. The subsequent recapture time of 50±10 fs is determined by directly monitoring the intensity change of the BGS and hot electrons in TRPES spectra. When a UV pump is employed, electrons are excited either from the BGS to a resonance in the CB, or from the top of the valence band (VB) to the bottom of the CB. The same trapping of hot electrons is observed as for infra-red excitation. In addition, a long lifetime component (>1 ps) of the hot electron decay and the BGS recovery are observed, pointing to trap assisted exciton recombination.

Scanning Probe Microscopy Focus Topic
Room: 10 - Session SP+AS+MI+NS+SS-TuM

Probing Chemical Reactions at the Nanoscale

Moderators: Tae-Hwan Kim, Pohang University of Science and Technology, Republic of Korea, Giang Nguyen, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

8:00am **SP+AS+MI+NS+SS-TuM1 Single Molecule Junction: Chemical Optimization of Charge Transport through Single Benzene Derivatives**, ***Parisa Yasini***, *S. Afsari, P. Pikma, E. Borguet*, Temple University

Single molecules are possible components of miniaturized electronic devices. Interconversion between states using external stimuli is a convenient way to generate single molecule devices such as switches and sensors. In this study, we have devised an electromechanical single molecule junction where molecular orientation is controlled by the working electrode potential in an electrochemical environment. We used the scanning tunneling microscopy (STM)-break junction method to measure the electrical properties of benzene derivatives, e.g., tetrafluoroterephthalic acid (TFTPA), terephthalic acid (TPA) and trimesic acid (TMA), bridged between two gold electrodes (the conducting substrate and STM tip). At potentials more negative than zero charge potential, direct contact between the π –system of a benzene ring and the Au (111) electrode results in the formation of a highly ordered monolayer and a high conductance of 0.24 G_o, 0.22 G_o and 0.15 G_o are detected for TFTPA, TPA and TMA, respectively. Moving to potentials more positive than the potential of zero charge triggers an order-disorder transition as revealed by STM. Our results show that charge transport through the π conjugated benzene ring increases by fluorination of TPA and decreases by an addition of a carboxylic acid functional group to the TPA. Accordingly, these results suggest that using functional groups, charge transport can be modified by manipulation of the electronic structure of molecules.

8:40am **SP+AS+MI+NS+SS-TuM3 How is Armchair Graphene Nanoribbon Oxidized?**, ***Chuanxu Ma***, *A.A. Puretzky, A.P. Baddorf,* Oak Ridge National Laboratory, *Z. Xiao, W. Lu,* North Carolina State University, *K. Hong,* Oak Ridge National Laboratory, *J. Bernholc,* North Carolina State University, *A.-P. Li*, Oak Ridge National Laboratory

The stability of graphene nanoribbons (GNRs) in air is crucial for practical applications. Here we study the temperature stability of the armchair GNR with a width of seven carbon atoms (7-aGNR) after exposed to air. Combining scanning tunneling microscopy, Raman spectroscopy, x-ray photoemission spectroscopy, and first-principles theory calculations, the oxidization of the armchair GNRs is found to start from the edges at ab out 520 °C, while below 430 °C the edges are unchanged. Two different types of oxygen species are atomically identified, specifically hydroxyl (OH) and atomic oxygen bridging two carbons, both of which are common oxygen forms in oxidized graphitic lattices. The bandgap is significantly reduced from 2.6 eV to 2.3 eV and 1.9 eV in the vicinity of hydroxyl or bridge O, respectively. Our results suggest that the oxidization will greatly affect the transport properties of GNRs. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

9:00am **SP+AS+MI+NS+SS-TuM4 Molecular Chessboard Assemblies Sorted by Site-Specific Interactions of Out-of-Plane d-Orbitals with a Semi-metal Template**, *T.A. Jung,* Paul Scherrer Institut (PSI), Switzerland, *A. Wäckerlin, S. Fatayer, T. Nijs, S. Nowakowska, S.F. Mousavi, O. Popova,* ***Aisha Ahsan***, University of Basel, Switzerland, *C. Wäckerlin*, Paul Scherrer Institut (PSI), Switzerland

We present a conceptually new approach for the formation of 2D chessboard patterns of molecules which is, unlike the other approaches, not dependent on the molecules being functionalized for self-assembly. The deposited Phthalocyanines (Pcs) are sorted in alternating sequence into the 2D layer by their site-specific interaction with the native reconstruction of the bismuth thin-film. The square p-(10 x 10) layer of bismuth on Cu(100) is characterized by the periodic arrangement of shallow pockets which are separated by rims and nodes which originate from the limited registry between Bi and Cu(100). The symmetry and the pitch of 1.8 nm of the Bi/Cu(100) substrate matches with the 4-fold symmetry of the Pc molecules and the pitch of a Pc chessboard arrangement.

We attribute the sorting mechanism to the site-specific interactions between the Bi layer and the out-of-plane 3d states of Mn- and CoPc leading to preferred adsorption sites. The 3d states also allow for the identification of the molecular components in the STM data: Mn and CoPc exhibit a bright contrast on the central metal atom, while Cu in CuPc in absence of such a d-state close to E_F is depicted as a depression.

Due to this characteristic difference in the 3d states, MnPc + CuPc and CoPc + CuPc sort into chessboard arrays. In these arrays, the molecules with out-of-plane 3d states (CoPc and MnPc) adsorb on the Bi-nodes and the one without (CuPc) adsorbs on the Bi-pores. If both molecules have out-of-plane 3d states around the Fermi level (CoPc + MnPc mixture), the selectivity of adsorption is insufficient and no chessboard layer is formed.

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11:20am **SP+AS+MI+NS+SS-TuM11 Nanoscale Chemical Analysis with Photo-induced Force Microscopy**, ***Sung Park***, Molecular Vista, Inc.

Infrared Photo-induced Force Microscopy (IR PiFM) is based on an atomic force microscopy (AFM) platform that is coupled to a widely tunable mid-IR laser. PiFM measures the dipole induced at or near the surface of a sample by an excitation light source by detecting the dipole-dipole force that exists between the induced dipole in the sample and the mirror image dipole in the metallic AFM tip. This interaction is strongly affected by the optical absorption spectrum of the sample, thereby providing a significant spectral contrast mechanism which can be used to differentiate between chemical species. Due to its AFM heritage, PiFM acquires both the topography and spectral images concurrently and naturally provides information on the relationship between local chemistry and topology. Due to the steep dipole-dipole force dependence on the tip-sample gap distance, PiFM spectral images have spatial resolution approaching the topographic resolution of AFM, demonstrating sub 10 nm spatial resolution on a variety of samples. PiFM spectral images surpass spectral images that are generated via other techniques such as scanning transmission X-ray microscopy (based on synchrotron source), micro confocal Raman microscopy, and electron microscopes, both in spatial resolution and chemical specificity. The breadth of the capabilities of PiFM will be highlighted by presenting data on various organic, inorganic, and low dimensional materials. By enabling imaging at the nm-scale with chemical specificity, PiFM provides a powerful new analytical method for deepening our understanding of nanomaterials and facilitating technological applications of such materials.

11:40am **SP+AS+MI+NS+SS-TuM12 STM Studies of the Molecule-2D Heterointerface**, ***Andrew Wee***, National University of Singapore, Singapore, *Y.L. Huang,* Institute of Materials Research & Engineering, Singapore, *Y.J. Zheng, Z.B. Song,* National University of Singapore, *S.Y. Quek*, Department of Physics, National University of Singapore **INVITED**

We have previously shown that the electronic and chemical properties of graphene can be controllably tuned via molecular functionalization [1]. In this talk, I will focus on our recent work on semiconducting 2D transition metal dichalcogenides (TMDs) with tunable direct bandgaps dependent on the number of atomic layers. We use high resolution scanning tunneling microscopy/spectroscopy (STM/STS) to study the atomic structure, intrinsic electronic properties, and grain boundaries of MoS_2 and WSe_2 layers on HOPG substrates [2,3]. Using PTCDA as a prototype semiconductor organic molecule, we show that a monolayer TMD can effectively screen an organic-inorganic heterointerface [4]. We have also studied how a $C_{60}F48$ molecular acceptor layer on top of a single-layer WSe_2 acts as p-type dopant, and reveal the electronic structure at a prototypical 1D interface between intrinsic and p-doped WSe_2 [5].

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Sustainability Focus Topic
Room: 5 & 6 - Session SU+AC+MI+MS-TuM

Critical Materials and Energy Sustainability
Moderators: Erik B. Svedberg, The National Academies, Robert Lad, University of Maine

8:00am **SU+AC+MI+MS-TuM1 How Critical Materials Affect Emerging Technologies**, ***Alexander King***, The Ames Laboratory **INVITED**

We live in a golden age for the development of technologies that have potential for clean and efficient production, storage or use of energy. Many, if not all of these technologies, however, depend on the properties of specific materials that may have low availability, or produce environmental challenges of their own during their production. We will look at the impact of materials supply challenges on the adoption of some recent clean energy technologies, consider possible impacts on some emerging technologies, and describe what efforts must be undertaken to ensure that fragile materials supply-chains do not prevent the adoption of technologies that promote a sustainable energy future.

9:20am **SU+AC+MI+MS-TuM5 The Role of Oxidation and Charging Rates on Li Electrochemical Deposition in Solid State Batteries**, ***Alexander Yulaev***, University of Maryland, *V. Oleshko*, NIST, *P. Haney*, NIST Center for Nanoscale Science and Technology, *A.A. Talin*, Sandia National Laboratories, *M.S. Leite*, University of Maryland, *A. Kolmakov*, NIST Center for Nanoscale Science and Technology

The recent progress in all-solid-state Li-ion batteries (SSLIBs) allowed a significant reduction of overall dimensions of stand-alone medical and micro-electronic devices. Owing to their compatibility with microfabrication process, high specific power, energy densities, and reduced safety risks of the thermal runaway, SSLIBs are likely to compete with their liquid counterparts in the near future. However, the large-scale implementation of SSLIBs requires further characterization during their fabrication and operation. Particularly, spatially resolved *in-operando* techniques probing electrochemical processes at the interfaces are needed. In the present work, we quantify the effects of oxidizing environment and charging rates on a lithium plating morphology using UHV electron microscopy and spectroscopy in correlation with electrochemical characterization. To conduct these measurements, we fabricate a model thin-film planar battery with $LiCoO_2$ cathode, LiPON electrolyte, and an ultra-thin carbon anode. Our experimental data reveal a strong dependence of plated Li morphology on presence of oxidation species at the surface and a gas phase. Under UHV conditions a linear correlation between the nucleation density of lithium clusters and a charging rate is observed. We show that the 2D nucleation model adequately describes the obtained dependence. The plated lithium morphology drastically changes from the in-plane clusters to out-of-plane whisker growth when ~10^{-7} Pa of oxygen is admitted to the UHV chamber. The in-plane cluster growth resumes when oxygen pressure increases from 10^{-7} to 10^{-5} Pa. We envision that our findings will contribute to whisker-free safer SSLIB performance under realistic operating conditions.

9:40am **SU+AC+MI+MS-TuM6 Unique Super-Ionicity Achieved on the Nanoscale with Applications in Next-Generation Lithium Ion Batteries**, ***Progna Banerjee***, *D. Dumett Torres*, *P. Jain*, University of Illinois at Urbana-Champaign

Lithium-ion (Li-ion) batteries have been dominating the global market for consumer electronics and power vehicles. However, significant safety concerns arise from degradation reactions (reduction/decomposition) of the electrolyte during cycling, potentially causing dendrite formation resulting in leakage and fires. A potential solution is the replacement of the flammable organic electrolyte with an inorganic solid electrolyte with superior electrochemical, mechanical and thermal stability, absence of leakage, long shelf-life, enhanced electrochemical stability and the possibility of battery miniaturization.

A promising candidate for these solid electrolytes are super—ionic materials which exhibit high ionic conductivities matching those of liquid electrolytes. In these materials, past a phase transition, one sub-lattice (often the cationic) melts, resulting in a disordered cation network, wherein cations can transport in a manner reminiscent of that of a liquid. Known superionic materials, such as AgI, Cu_2Se etc. in their bulk form, display this phase transition at high temperatures and/or pressures, making them unsuitable for many applications. In our recent study, we examined Cu_2Se nanocrystals (NCs) prepared from their magic-sized CdSe counterparts using a synthetic topotactic method called cation exchange. In these NCs, the superionic disordered "liquid-like" behavior was observed under ambient conditions. Larger NCs prepared under similar conditions interestingly display ordered layers of Cu^+ ions and vacancies similar to bulk solid. We investigate the origin of this nanoscale effect using arguments based on lattice strain, cationic occupancies obtained from crystallography, and density functional theory (DFT) calculations.

We are extending this work to investigate the possible mechanism of ionic transport in these NCs using a.c. impedance measurements. We are investigating size and dimensionality effects on the transport behavior of cations and the superionic phase transition. We will also investigate the effect of cation vacancies in terms of their profile and density on the phase transition behavior and ionic conductance. This study will pave the way to fundamental understanding on ion transport behavior in solids, and applications as solid-state electrolytes, thermoelectrics and ultrafast electronic switches.

11:00am **SU+AC+MI+MS-TuM10 Electric Cell Potential Driving Changes in Perovskite Surface Termination and Enabling Catalysis**, ***Monika Backhaus***, Corning, *L. Gregoratti*, *M. Amati*, Elettra-Sincrotrone Trieste, Italy **INVITED**

Dynamic segregation processes in perovskite electrodes have been studied in operando in electrochemical model cells with thin zirconia electrolyte and mixed perovskite catalyst by spatially resolved scanning photoelectron microscopy (SPEM) in combination with impedance spectroscopy and gas analysis in the goal to gain better understanding of electrode surface chemistry and its key drivers. We focused on the oxygen reduction reaction at perovskite electrodes and electrochemically driven reactions, such as redox reactions in chemical reactors or sensors. The current overview summarizes our synchrotron in-operando surface spectroscopy in various technical areas.

Our electrochemical cells are built of a thin zirconia electrolyte and mixed perovskite catalyst. They were studied by SPEM at the Elettra synchrotron. The experimental set up allowed operating temperatures up to 700C, mixtures of unreactive or reactive gases at chamber pressure up to 10^{-5} mbar and local pressure above the sample of 1mbar (gas jet). Electrochemical measurements, such as monitoring of i-V behavior or impedance were realized simultaneously.

The surface termination of $(La,Sr)MnO_3$ (LSM) electrodes was studied as a function of cell potential, oxygen partial pressure and temperature. The surface chemistry reversibly changed with applied potential, exhibiting Mn-termination in highly oxygen-rich environment and increasing strontium segregation in oxygen-poor environment and under reducing cell potential. Cathode termination changed not only with applied cell potential, but also with cell current. LSM cathode pump cells operating at high current densities preserved an "oxygen-rich" surface chemistry under high cell potential, while low current cells exhibited large changes in surface chemistry.

The response of perovskite electrodes to reactive gas environment was also investigated. Model cells with LSM electrodes were studied in oxygen-propene gas mixtures at different cell potentials under oxygen flux at 400-600°C. Oxygen ion flux and cell potential, both were found to drive dynamic changes of catalyst and electrolyte surface chemistry, including redox reaction, surface segregation and long range surface diffusion. Strongly positive cell potential drove an interaction of hydrocarbon with the mixed oxide catalyst surface, yielding adsorbed carboneous species with epoxy-type bonding at a strongly Sr-enriched surface. The carboneous surface complexes reversibly formed and decomposed with cell potential, suggesting it to play the role of an intermediate in an oxide-electro-catalyzed partial oxidation of propene.

11:40am **SU+AC+MI+MS-TuM12 Possibilities of Hydrogen Energy Utilization in Kazakhstan: Preparation of TiCrMn Hydrogen Storage Alloys and Investigation of Their Absorption Properties**, ***Saule Zholdayakova****, H.-H. Uchida, Y. Matsumura*, Tokai University, Japan

The society of Kazakhstan has been becoming strongly dependent on fossil fuels, which results in facing serious environmental problems. Kazakhstan is a Central Asian country with rich natural resources, such as Mn, Cr and Ti and energy self-sufficiency is 200% including exportation. Most of the consumption is fossil resources, mainly dependent on coal. The power configuration of Kazakhstan is 70% coal, 19% natural gas, 1% oil, and 10% hydraulic power. With a background of rich production of fossil fuels, Kazakhstan exports most of its oil and domestically dependent on coal. By 2020, Kazakhstan government planning to reduce the amount of green house gas produces by 15% of that in 1992. For these reasons, the development of renewable energy is significant. In this study we focus on the application of hydrogen as an energy carrier for spreading renewable energy, especially hydrogen energy to solve the environmental problems in Kazakhstan. Hydrogen has more energy per unit of mass, flexible storage options, and it is clean energy. Hydrogen can be stored as a gas, a liquid and as a solid. The other side, for realization hydrogen energy system we need to think more concretely about a manufacture of hydrogen, storage, transportation and utilization. The main manufacture method for hydrogen is electrolysis. The electricity consumption per capita is 5000 kWh/year. If hydrogen energy become a conductor of energy, 1.13m^3/year of water will necessary to source of hydrogen. After utilizing renewable energy for product hydrogen from water, storage, transport and change to electric power. In the end of consumption, we get the same amount of water. In this study, especially conditions necessary for the renewable energy in Kazakhstan are summarized and trained to preparing hydrogen storage ally using the metals of Mn, Cr and Ti available in Kazakhstan.

Actinides and Rare Earths Focus Topic
Room: 22 - Session AC+MI+SA+SU-TuA

Actinide and Rare Earth Theory
Moderator: Ladislav Havela, Charles University, Prague, Czech Republic

2:20pm **AC+MI+SA+SU-TuA1 Magnetic Susceptibility, Magnetic Resonance, and Bonding in Actinide Complexes: Ab-initio Calculations**, ***Jochen Autschbach***, University of Buffalo, SUNY **INVITED**

Actinide complexes exhibit fascinating magnetic properties and interesting chemical bonding. An on-going research project in our group is devoted to first-principles calculations of magnetic resonance parameters (NMR, EPR), magnetic susceptibilities, and other spectroscopic parameters of actinide complexes in relation to their chemical bonding, in particular regarding the involvement of the 5f shell in metal-ligand bonding. We will present results from recent computational studies of magnetic resonance parameters and the magnetic susceptibility of f-element complexes utilizing relativistic quantum chemical methods.

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3:00pm **AC+MI+SA+SU-TuA3 Combining DMRG with Standard Relativistic Multireference Methods to Probe the Properties of Strongly Correlated Systems: Plutonium Oxides**, ***Valérie Vallet***, *S. Kervazo,* CNRS / University of Lille, France, *F. Réal,* University of Lille, France, *A. Severo Pereira Gomes,* CNRS / University of Lille, France, *F. Virot*, IRSN, France **INVITED**

Actinide-containing complexes present formidable challenges for electronic structure methods due to the large number of degenerate or quasi-degenerate electronic states arising from partially occupied 5f and 6d shells. In particular, we focus our study here on volatile forms of plutonium such as PuO_2, PuO_3 or $PuO_2(OH)_2$, for which spectroscopic and thermodynamics properties are of interest.

To attain an accuracy comparable to that of experiments, highly accurate calculations including static and dynamic correlation effects as well as relativistic effects are required. Conventional multi-reference methods, however, can treat active spaces that are often at the upper limit of what is required for a proper treatment of species with complex electronic structures and large number of valence orbitals involved in chemical bonds, leaving no room for verifying their suitability.

In this work, we address first the issue of properly defining the active spaces in such calculations, and introduce a protocol to determine optimal active spaces based on the use of the Density Matrix Renormalization Group algorithm and concepts of quantum information theory.[1]

The guidance offered by this protocol allows us to define the suitable active space to compute the electronic structures

and the nature of the ground states with the desired accuracy, i.e. the clear multi-reference character of the wave-function of those compounds requires that the energies of formation to be computed with multi-configurational quantum chemical methods like CASSCF and CASPT2 and with spin-orbit interaction, treated here *a posteriori* with the state-interaction RASSI method. Specifically, our results illustrate the complex multi-configurational character of PuO_3. The computed thermodynamics quantities reach a high accuracy allowing us to predict the composition of the released volatile products.

5:00pm **AC+MI+SA+SU-TuA9 The Thermal Expansion of UC and UO_2 from First Principles Calculations - The Importance of Correlations Effects and Spin-orbit Coupling**, ***Dominik Legut***, IT4Innovations Center, VSB - Technical University of Ostrava, Czech Republic, *U.D. Wdowik*, Pedagogical University, Poland, *P. Piekarz,* Polish Academy of Sciences, Poland, *G. Jaglo*, Pedagogical University, Poland, *L. Havela*, Charles University, Prague, Czech Republic

Uranium monocarbide, a potential fuel material for the generation IV reactors, is investigated within density functional theory. Its electronic, magnetic, elastic, and phonon properties are analyzed and discussed in terms of spin-orbit interaction and localized versus itinerant behavior of the 5*f* electrons. We demonstrate that the theoretical electronic structure, elastic constants, phonon dispersions, and their densities of states can reproduce accurately the results of x-ray photoemission and bremsstrahlung isochromat measurements as well as inelastic neutron scattering experiments only when the 5*f* states experience the spin-orbit interaction and simultaneously remain partially localized [1]. The partial localization of the 5*f* electrons could be represented by a moderate value of the on-site Coulomb interaction parameter of about 2 eV. The results of the present studies indicate that both strong electron correlations and spin-orbit effects are crucial for realistic theoretical description of the ground-state properties of uranium carbide. This is even more pronounced considering the thermal expansion and thermal conductivity of UC, where for the latter the optical phonon branches may cause a significant contributions [2]. We compare the novel material UC to the experimental data and to the presently used nuclear fuel material, UO_2 oxide. Here our calculations show that considering the exchange and electron correlations effects the generalized gradient approximation was successful in describing the phonon dispersion spectrum, thermal expansion, and heat capacity w.r.t to the recorded data [3]. For both materials the so-called direct method, based on the harmonic and quasi-harmonic approximation, was used [4]. To study the pressure dependence of the phonon frequencies of UO_2 we calculated phonon dispersions for several lattice constants. Our computed phonon spectra demonstrate the opening of a gap between the optical and acoustic modes induced by pressure. Taking into account the phonon contribution to the total free energy of UO_2 its thermal expansion coefficient and heat capacity have been computed from first-principles [3].

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Biomaterial Interfaces Division
Room: 12 - Session BI+AS+MI+SA-TuA

Bio from 2D to 3D: Challenges in Fabrication and Characterization & Flash Presentations
Moderators: Lara Gamble, University of Washington, Anna Belu, Medtronic

2:20pm **BI+AS+MI+SA-TuA1 Cell-instructive Polymer Matrices for Therapies and Tissue Models**, ***Carsten Werner***, Leibniz Institute of Polymer Research Dresden and TU Dresden, Deutschland **INVITED**

Sulphated and non-sulphated glycosaminoglycans (GAGs) can be instrumental in biomedical technologies beyond. In particular, incorporation of GAGs into biomaterials has been demonstrated to allow for the biomimetic modulation of growth factor signaling, providing control over therapeutically relevant cell fate decisions in various different settings. In an attempt to systematically explore the related options, we have introduced a rational design strategy for biology-inspired hydrogels based on multi-armed poly(ethylene glycol), GAGs and peptides (1,2,3). The theoretically predicted decoupling of biochemical and mechanical gel properties was confirmed experimentally and applied for implementing GAG-based biofunctionalization schemes to afford cell adhesiveness and morphogen presentation. A number of applications of customized GAG-based materials will be given, including inflammation-modulating wound dressings (3), cryogel particles to support cell replacement in Parkinson’s disease (4) and gel matrices to enable tissue and disease *in vitro* models for cancer biology (5,6) and nephrotoxicity studies. In sum, our reported approach demonstrates the power of joint theoretical and experimental efforts in creating bioactive materials with specifically and independently controllable characteristics (7).

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3:00pm **BI+AS+MI+SA-TuA3 Plant Virus Particles for 2D and 3D Architectures on Surfaces**, *V. Rink,* University of Kaiserslautern, Germany, *M. Braun,* RLP Agroscience GmbH, Germany, *M. Ani,* University of Kaiserslautern, Germany, *K. Boonrood,* RLP Agroscience GmbH, Germany, *C. Müller-Renno,* University of Kaiserslautern, Germany, *G. Krczal-Gehring,* RLP Agroscience GmbH, Germany, ***Christiane Ziegler***, University of Kaiserslautern, Germany

Biohybrid materials consist of biological entities and artificial, often inorganic materials. These biohybrids may be used in many fields of applications, ranging from biosensors to implant materials. In this context, bottom-up approaches, in which small elementary building blocks of matter are used to form larger elements through self-assembly have gained a lot of interest.

Plant viruses are promising candidates for such building blocks. Because of their simple structure and pre-defined size and form they have a high potential for self-assembly. Furthermore they can be genetically manipulated to create new functionalities by extending the capsid with different side chains.

We could show that unspecific electrostatic interactions govern the formation of large ordered 2D structures of self-assembled icosahedral tomato bushy stunt virus (TBSV) particles. By adding amino acid side chains to the capsid subunit the isoelectric point of the virus is changed. Thus by the right combination of virus modification, substrate and pH (and as a minor effect ionic strength) one can control the dimensions of 2D virus islands which may form layers with macroscopic dimensions. Specific structures in these 2D layers may be introduced by substrates which are pre-structured, e.g. by nano imprint lithography.

In addition to the electrostatic control the amino acid side chains allow also more specific interactions. Examples are histidine side chains interacting with Ni ions or gold binding peptide side chains with Au. With these specific interactions, also the third dimension is accessible. This opens the possibility to play with viruses in a kind of nano Lego which will soon become reality.

In this contribution we will show a scanning force and scanning electron microscopy study of the self-assembly of 2D and 3D structures of TBSV on Si and mica surfaces. The three dimensional structure is based on a homogeneous layer consisting of virus-particles carrying additional 4xAsp6xHis side chains (lowest stack). For the following second stack the chemical selectivity of these side chains to Ni ions (here: Ni-nitrilotriacetic acid (Ni-NTA) carrying a 5 nm Au nanoparticle was utilized. Au-binding virus-particles interact with these Au particles and create the third stack of this 3D virus architecture. The success of this strategy could be proven by SFM height measurements which reveal a height in the range of 66 nm, which corresponds to two layers of virus particles (30 nm each) coupled by Ni-NTA.

Lüders et al. (2012). Tomato bushy stunt viruses (TBSV) in nanotechnology investigated by scanning force and scanning electron microscopy. *Colloids Surf. B91*, 154

3:20pm **BI+AS+MI+SA-TuA4 Designing Thermo-responsive Nanocomposites that Provides Multiple Defense Mechanisms against Fouling**, ***Ya Liu***, University of Pittsburgh, *C. Zhang, S. Kolle, J. Aizenberg,* Harvard University, *A.C. Balazs*, University of Pittsburgh

We use computational modeling to design synthetic gel-based composite coatings that provide multiple defense mechanism against the fouling of the underlying substrate. The system encompasses rigid posts embedded in a lower critical solution temperature (LCST) thermo-responsive gel, which swells at lower temperatures and collapses at higher temperatures. By developing new dissipative particle dynamics (DPD) simulationd that capture the cell-surface interactions , we exam the biofilm growth and structure development on the substrates and pinpoint the parameter space that yields the optimal antifouling behavior for this system. The advantage of our approach relies on physical mechanisms and doesn't have unwanted environmental consequences.

4:20pm **BI+AS+MI+SA-TuA7 3D Ink-jet Printing for Tissue Engineering**, ***Thomas Boland***, The University of Texas at El Paso **INVITED**

An inkjet application is described, where biologically active ink, which may include drugs and living cells as well as non-active can be deposited alongside scaffolding materials to build two- and three-dimensional constructs for medical treatment. The technology faces several limitations that present interesting engineering opportunities. The nature and scope of the problems will be discussed in the context of the fabrication of microvasculature. The current tissue engineering paradigm is that successfully engineered thick tissues must include vasculature. As biological approaches alone such as growth factors have fallen short of their promises, one may look for an engineering approach to build microvasculature. Layer-by-layer approaches for customized fabrication of cell/scaffold constructs have shown some potential in building complex 3D structures and with the advent of cell printing, one may be able to build precise human microvasculature. Several research projects will be presented. The fabrication of microvsculatures for skin and adipose tissue engineering and current studies to characterize the biology and functionality of these engineered structures will be presented. These data suggests that a combined simultaneous cell and scaffold printing can promote microvasculature formation and improve current tissue engineering technology.

5:00pm **BI+AS+MI+SA-TuA9 Digging for Answers: Challenges in ToF-SIMS Tissue Depth Profiling**, ***Daniel Graham***, *T.B. Angerer, L.J. Gamble*, University of Washington, Seattle

The advent of cluster ion beams for time-of-flight secondary ion mass spectrometry (ToF-SIMS) instrumentation has opened up many opportunities for depth profiling organic samples. Combined with its high lateral resolution imaging capabilities, SIMS can provide 3D imaging information from a wide range of organic materials including cells and tissues. The ability to track chemical changes both across and throughout tissue sections could help identify molecular changes related to targeted drug delivery or disease states in the cellular micro-environment. While there have been many studies showing the utility of ToF-SIMS depth profiling for polymer materials, similar studies with cells and tissues have been limited. This has likely been due to the challenges encountered when working with biological samples. It has been shown that one can depth profile cells as long as the levels of buffer salts and other inorganic components is minimized. Similar work with depth profiling tissues has been limited. Herein we will present our findings on the challenges of depth profiling tissues and discuss ways these challenges may be avoided. Examples will be shown using both single beam argon cluster depth profiling and dual beam depth profiling using Bi3+ for analysis and argon clusters for sputtering. In general a significant loss in signal is seen after the first few layers of a tissue depth profile. This could be due to migration of components to the surface, ion beam damage, or ion suppression due to salts. In spite of these issues, tissue depth profiles can be acquired in most cases. The challenge then becomes processing and interpreting these large data sets. Ideas on how to overcome these challenges will be presented.

5:20pm **BI+AS+MI+SA-TuA10 Cryo-SIMS – Metrology of Biological Sample Preparation Methods for Preservation of Cell Ultrastructure and Chemistry**, ***Paulina Rakowska***, *J.-L. Vorng, I.S. Gilmore*, National Physical Laboratory, UK

With the potential of high-throughput, high-resolution and high-sensitivity label-free imaging in 3D, secondary ion mass spectrometry imaging methods are, arguably, ones of the most powerful techniques for high-resolution chemical imaging of biological samples. However, there are some critical limitations for these analyses. As the high-performance SIMS instruments require high vacuum, a careful consideration of sample preparations is often needed. For example, advanced methods are necessary to prepare and measure complex hydrated bacterial biofilm structures. Also, in the pharmacological imaging of potential drug candidates at their targets, the positioning of water soluble drug compounds within cells or tissues can be altered by pre-treatment processes such as drying, resin-embedding or histological fixation. Advanced cryo-preparation methods are necessary for immobilisation of water in these samples to prevent the ultrastructural reorganisation and the loss or translocation of water-soluble molecules, to circumvent the use of chemical fixation and to enable their analysis in high-vacuum of mass spectrometry instruments.

The UK's National Centre of Excellence in Mass Spectrometry Imaging (NiCE MSI) at NPL has a special focus on the development of advanced solutions to challenging measurements. Our recently innovated 3D

OrbiSIMS instrument has the capability to handle and measure cryogenically-prepared samples. The instrument is equipped with a vacuum cryo transfer system that is compatible with cryo-SEM and cryo-TEM. A shuttle chamber allows the interchange of samples, in vacuum and cryogenically, between cryo-preparative equipment and the 3D OrbiSIMS instrument.

This presentation will show our recent developments of the cryo-SIMS methodologies. Different sample cryo-preparation techniques will be compared, such as the analysis performed on frozen-hydrated vs. frozen-dehydrated mammalian cells. The application of cryo-SIMS to a range of biological samples including cells, bacteria, biofilms and organic reference samples will be presented. Focus will be given to the use of different types of cryo-protectants, often required for the vitrification of thicker samples such as biofilms, by high-pressure freezing and their effects on SIMS analysis.

5:40pm **BI+AS+MI+SA-TuA11 Towards Cryogenic 3D Nano-XRF Imaging of Biological Samples**, ***Axel Rosenhahn***, *S. Stuhr, C. Rumancev, T. Senkbeil, T. Gorniak, A. von Gundlach, J. Reinhardt,* Ruhr-University Bochum, Germany, *Y. Yang, P. Cloetens,* ESRF, France, *M. Grunze,* Karlsruhe Institute of Technology (KIT), Germany, *J. Garrevoet, G. Falkenberg, W. Schröder*, DESY, Germany

Nanoprobe X-ray fluorescence (nano-XRF) analysis allows spatially resolved imaging with chemical sensitivity. Approaching the diffraction limit at the next generation of storage rings, both, spatial resolution and brilliance are going to be strongly enhanced for nano-XRF experiments. For biological samples, the combination of nano-XRF with cryogenic sample environments allows to understand elemental distributions in cells with minimum preparation artefacts. In addition, the cryo-protected samples provide enhanced resistance against radiation damage, which is particularly important for the high photon densities at modern synchrotron sources. Three different applications of cryo-nano-XRF will be presented. For single melanosomes, the technique enabled us to prove the core-shell organization of the organelles using metals as surrogate markers. As second application, the distribution of metals in single, adherent cells was directly imaged without the requirement of additional markers. Finally, marine adhesives of diatoms were analyzed and the occurrence of metals are linked with the known organic constituents in the EPS of diatoms. In all three cases, the detection of metal distribution has provided a new view on the investigated samples. The cryogenic sample environments proved to be the key to apply synchrotron radiation to all three types of biological samples. The data will also be discussed in relation to the perspectives of new implementations that will enable fast cryo-3D imaging in the future.

Magnetic Interfaces and Nanostructures Division Room: 11 - Session MI+2D+AC+NS-TuA

Spin-Orbit Phenomena at Surfaces and Interfaces

Moderators: Markus Donath, Westfälische Wilhelms-Universität Münster, Germany, Axel Hoffmann, Argonne National Laboratory

2:20pm **MI+2D+AC+NS-TuA1 Coherent Control over Spin-polarized Dirac Surface State in Topological Insulators**, ***Kenta Kuroda***, The Institute for Solid State Physics, The University of Tokyo, Japan **INVITED**

A number of challenging efforts have been recently made for a coherent control of highly spin-polarized Dirac surface states in various topological insulators, suggesting ultrafast optospintronic devices. However, these attempts generally neither realized a selective photoexcitation of the surface state, since the optical response is typically governed by the bulk properties, nor do they exclusively probe the excitation of the surface state, because the applied techniques are not surface sensitive.

In my talk, I will report that the difficulty can be overcome by direct band mapping of a photoexcitation in the Dirac surface state with time-resolved two-photon photoemission spectroscopy combined with ultrashort tunable pump pulses in mid-infrared regime. It is revealed that the mid-infrared excitation permits a direct population of the unoccupied Dirac-cone owing to a novel optical coupling across the Dirac point. In addition, the direct optical transition induces a pronounced asymmetry of the transient surface population in *k*-space which indicates an excitation of a net spin-polarized photocurrent even with linear pump polarization [Phys. Rev. Lett. **116**, 076801 (2016)]. Moreover, the pump polarization can control the asymmetric population, *i.e.* the surface photocurrent, through the coherent optical transition of the surface Dirac-cone [Phys. Rev. B **95**, 081103(R) (2017)]. By observing the decay of the asymmetric population, the ultrafast dynamics of the photocurrent in the surface Dirac-cone is directly investigated. Our discovery promises important advantages of photoexcitation by mid-infrared pulses for optspintronic applications.

3:00pm **MI+2D+AC+NS-TuA3 Enhancement of Voltage-Controlled Magnetic Anisotropy Through Metallic Insertion at the CoFeB|MgO Interface**, ***Kevin Fitzell***, *X. Li, C.T. Karaba, A. Buditama, G. Yu, K. Wong,* University of California at Los Angeles (UCLA), *D. Wu,* UCLA; Fudan University, Republic of China, *N. Altieri, C. Grezes,* UCLA, *N. Kioussis,* CSU, Northridge, *S.H. Tolbert*, UCLA, *Z. Zhang*, Fudan University, Republic of China, *J.P. Chang, P.K. Amiri, K.L. Wang*, UCLA

Paramount to the continued scaling of MRAM devices is a comprehensive understanding and control of the factors affecting the interfacial phenomena that occur at the CoFeB|MgO interface, from which the perpendicular magnetic anisotropy (PMA) of the CoFeB originates. Efficient manipulation of this PMA using an applied voltage, known as the voltage-controlled magnetic anisotropy (VCMA) effect, offers significant energy savings over electric-current-controlled alternatives such as STT-RAM. *Ab initio* studies in the literature on Fe/MgO interfaces revealed a dependence of the VCMA effect on the oxidation state of interfacial Fe atoms[1] and on the addition of various heavy metal insertion layers[2] at the CoFeB/MgO interface. While this effect of metallic insertion layers at the CoFeB/MgO interface has not been extensively studied experimentally, inserting a thin Mg layer at the CoFeB/MgO interface has been shown in the literature to improve the (001) texture of the MgO, the tunneling magnetoresistance (TMR) ratio of the MTJ, and the thermal stress stability of the CoFeB layer's PMA.[3,4] What is lacking in the literature, however, is experimental work studying the dependence on the VCMA effect of Mg insertion layers at the CoFeB/MgO interface.

In this work, the impact of several types of metallic insertion layers (Ta, Pt, and Mg) at the CoFeB|MgO interface on the VCMA characteristics and other magnetic properties is studied. For the case of Mg insertion, four different regimes of materials properties were observed, corresponding to the oxidation state at the CoFeB|MgO interface. Inserting an ultrathin Mg layer of 0.1–0.3 nm yielded a VCMA coefficient of ~100 fJ/V×m, representing more than a factor of 3 improvement over average values of ~30 fJ/V×m reported in Ta|CoFeB|MgO-based structures. Ultrathin Ta and Pt insertion layers also showed a small improvement, yielding VCMA coefficients around 40 fJ/V×m. Electrical, magnetic, and synchrotron-based X-ray diffraction results reveal that a 1.1–1.3 nm Mg insertion layer gives rise to the highest perpendicular magnetic anisotropy and saturation magnetization, as well as to the best CoFe and MgO crystallinity; Mg insertion layers thicker or thinner than this give rise to either under- or over-oxidation of the CoFeB|MgO interface. These results demonstrate that precise control over the oxidation level at the CoFeB|MgO interface is crucial for the development of electric-field-controlled perpendicular magnetic tunnel junctions with low write voltage.

3:20pm **MI+2D+AC+NS-TuA4 THz Radiation Generated from Interfacial Rashba Spin-orbit Coupling**, *M.B. Jungfleisch,* Argonne National Laboratory, *Q. Zhang,* Argonne National Laboratory, *W. Zhang,* Oakland University, *J.E. Pearson, H. Wen,* ***Axel Hoffmann***, Argonne National Laboratory

Electromagnetic terahertz (THz) radiation is a versatile tool for a wide variety of sensing technologies ranging from security systems to medical applications. Commonly THz radiation is generated using semiconducting materials and using their inherent charge dynamics. Recently, it was also demonstrated that optical excitation of fast spin current pulses in magnetic materials may generate strong broadband THz radiation from transverse spin transport phenomena, known as spin Hall effects. These experiments rely on a bulk conversion of spin currents into charge current, which then subsequently generate the THz radiation. Here we investigate whether interfacial spin-orbit coupling phenomena may also be an efficient source for generating THz radiation. For this purpose we combine a bilayer of Ag and Bi, which is known to have strong Rashba-type spin-orbit coupling at its interface with a magnetic CoFeB layer. Upon optical excitation we also observe in this system THz radiation. Additional experiments with individual Ag and Bi layers show that this radiation originates from interfacial spin galvanic effects. Furthermore, we demonstrate that the amplitude of the THz radiation varies with the helicity of the incident optical light pulse. These observations open up new perspectives for the development of ultrafast spintronic devices.

This work was supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division. Lithographic patterning was carried out at the Center for Nanoscale Materials, which is supported by DOE, Office of Science, BES (#DE-AC02-06CH11357).

4:20pm **MI+2D+AC+NS-TuA7 Spin-orbit Coupled d-electron Surface States of Delafossite Oxides**, ***Phil King***, University of St Andrews, UK **INVITED**

The ABO$_2$ family of delafossite oxide metals has recently found renewed prominence due to their remarkable transport properties. The Pd- and Pt-based cobaltates are the most conductive oxides known, with room-temperature resistivities lower per carrier even than copper metal [1,2]. Meanwhile, giant low-temperature mean-free paths of up to 10^5 lattice spacings make hydrodynamic effects of the electron fluid observable in mesoscopic samples [3] and lead to a curious negative longitudinal magnetoresistance [4]. This is all underpinned by extremely broad bandwidths of the bulk electronic structure around the Fermi level, dominated by Pd/Pt-derived carriers that behave remarkably like free electrons [2], in part mediated by an unusual interplay with correlations which renders the Co block insulating. The crystal structure is polar, however, opening the potential for their surface electronic structures to be dramatically different to that of the bulk [5,6]. Here, we will show how these surfaces support strongly spin-split electronic states, and discuss the intriguing interplay of spin-orbit coupling and electronic interactions that they host.

Key collaborators on this work include Veronika Sunko (St Andrews and Max-Planck Institute for Chemical Physics of Solids, Dresden), Federico Mazzola (StA), and Helge Rosner, Pallavi Kushwaha, Seunghyum Khim, and Andy Mackenzie (MPI-CPFS).

[1] Hicks *et al.*, Phys. Rev. Lett. 109 (2012) 116401

[2] Kushwaha *et al.*, Science Adv. 1 (2015) e1500692

[3] Moll *et al.*, Science 351 (2016) 6277

[4] Kikugawa *et al.*, Nature Commun. 7 (2016) 10903

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5:00pm **MI+2D+AC+NS-TuA9 Understanding the Interfacial Interaction and Isotope Effects in Organic Spin Valve Structures**, ***Alexandra Steffen***, *N. Herath, J. Keum, H. Zhang, K. Hong, J. Jakowski, J. Huang, J. Browning, C.M. Rouleau, I.N. Ivanov, V. Lauter*, Oak Ridge National Laboratory

Spin-dependent phenomena, such as the extended spin relaxation time and spin diffusion length due to the very week spin-orbit coupling found in organic spin valves (OSV), are of interest from the view of both fundamental research and development of low power spintronic devices.

While deuteration is widely used for contrast variation measurements under the assumption that the deuterated structure shows identical characteristics in comparison to the protonated version, recently, strong isotopic effect on optoelectronic properties was reported and a remarkable reduction in the open circuit voltage was found [1].

In OSV systems, the interfacial properties are crucial for the understanding of the origin of the macroscopic properties. Still, to identify the exact behavior of the interfaces remains challenging, especially for buried soft matter/hard matter interfaces. Here, we utilize via Polarized Neutron Reflectometry to study depth-resolved the magnetic and chemical structure.

Our system under investigation are prototype spintronic devices with LSMO/polymer/Co trilayer structure, where polyfluorene (PFO) is selected as an optimal ‘hole’ conducting polymer through the model pre-screening based on the electron affinity and electron’s effective mass values obtained from theoretical calculations. Using the exceptional syntheses and deuteration capabilities we have recently completed syntheses of four PFO isotopes, i.e., protonated (P), main-chain deuterated (MD), side-chain deuterated (SD) and fully deuterated (FD) PFOs. By creating such modified polymers, the subatomic, intermolecular and interfacial interactions are modified and characteristics like the π-π interaction become tunable. For neutron scattering experiments, the nuclear cross-section varies with the isotopic substitution, thus via changing the contrast with chain-specific deuteration, different parts of a sample are investigated individually.

While our main goal is the understanding the effect of deuterium substitution on the spin-dependent electron transport, in this presentation, we will focus on the details of the structural and magnetization profiles on both LSMO\polymer and polymer\Co interfaces and their impact on the coupling between magnetic layers. We will present the results obtained via Polarized Neutron Reflectometry and discuss the interpretation of the depth-resolved magnetometry study.

[1] Ming Shao *et al.*, The isotopic effects of deuteration on optoelectronic properties of conducting polymers. *Nature Communications*, 5:3180, January 2014.

5:20pm **MI+2D+AC+NS-TuA10 Dispersion and Spin Structure of Conduction Bands of Single-layer TMDC's on Au(111)**, ***Philipp Eickholt****, *M. Holtmann,* Westfälische Wilhelms-Universität Münster, Germany, *C.E. Sanders, M. Dendzik, M. Bianchi, P. Hofmann,* Aarhus University, Denmark, *M. Donath,* Westfälische Wilhelms-Universität Münster, Germany

In the field of 2D materials, single-layer transition metal dichalogenides, especially MoS$_2$, WS$_2$, MoSe$_2$ and WSe$_2$, play an important role. Due to their exceptional optical and electronic properties, they are promising materials for optoelectronical applications [1]. The key to understand the material properties is a profound knowledge of the electronic structure. While the occupied electronic structure was investigated in a number of studies, the crucial information about the dispersion and spin structure of the conduction bands is still missing.

Spin- and angle-resolved inverse photoemission (SRIPE) [2] is the ideal technique to study dispersion and spin structure of the unoccupied electronic bands. In this talk, we present a SRIPE study of the conduction bands of single-layer WS$_2$ [3] and MoS$_2$ [4] grown on Au(111).

The focus of the presentation will be on the lowest conduction band near the K valley, which is decisive for the optoelectronic properties of the materials. The results will be discussed in consideration of a recent pump-probe (TR-ARPES) experiment [5], which determined the band gap of the “pumped” system.

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[3] M. Dendzik *et al.*, Phys. Rev. B **92**, 245442 (2015)

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5:40pm **MI+2D+AC+NS-TuA11 Unraveling the Spin Structure of Unoccupied States in Bi$_2$Se$_3$**, ***Markus Donath***, *C. Datzer, A. Zumbülte,* Westfälische Wilhelms-Universität Münster, Germany, *J. Braun,* LMU München, Germany, *T. Förster, A.B. Schmidt,* Westfälische Wilhelms-Universität Münster, Germany, *J. Mi, B. Iversen, P. Hofmann,* Aarhus University, Denmark, *J. Minár,* University of Pilzen, Czech Republic, *H. Ebert,* LMU München, Germany, *P. Krüger, M. Rohlfing,* Westfälische Wilhelms-Universität Münster, Germany

In topological insulators, spin-orbit coupling leads to the emergence of metallic topological surface states crossing the fundamental band gap. The optical control of spin currents in topological surface states opens new perspectives in (opto-) spintronics. To understand these processes, a profound knowledge about the dispersion and the spin polarization of both the occupied and the unoccupied electronic states is required. We present a joint experimental and theoretical study on the unoccupied electronic states of the topological insulator Bi$_2$Se$_3$ [1]. We discuss spin- and angle-resolved inverse-photoemission results in comparison with calculations for both the intrinsic band structure and, within the one-step model of (inverse) photoemission, the expected spectral intensities. This allows us to unravel the intrinsic spin texture of the unoccupied bands at the surface of Bi$_2$Se$_3$.

[1] Datzer *et al.*, Phys. Rev. B **95**, 115401 (2017)

Scanning Probe Microscopy Focus Topic
Room: 10 - Session SP+AS+MI+NS+SS-TuA

Probe-Sample Interactions
Moderator: Carl Ventrice, Jr., SUNY Polytechnic Institute

2:20pm **SP+AS+MI+NS+SS-TuA1 Atomic Manipulation of Atomic Oxygen on Graphene**, *H.K. Kim, T. Ahn, T.S. Youn, D.G. Lee,* ***Tae-Hwan Kim***, Pohang University of Science and Technology, Republic of Korea

Graphene, a single sheet of *sp*^{2}-bonded carbon atoms, is considered as a promising material for future electronic devices especially due to its superior electron mobility as well as mechanical stability. For various applications of graphene, however, the electronic structure has to be tuned and the diverse functionalization is strongly required. In particular, it has been well known that the oxidation of graphene can alter its electronic and optical properties remarkably. We have investigated the atomic oxygen chemisorbed on the epitaxial graphene using scanning tunneling microscopy (STM). The high-resolution topographic images and tunneling spectroscopy spectra reveal distinctive electronic states of oxygen atoms, which bridge two adjacent carbon atoms and make graphene epoxide. More importantly, using the STM tip can controllably induce the local removal and the rearrangement of the

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* **Falicov Student Award Finalist**

atomic oxygen by applying the appropriate biases. The technique is similar to the STM nanolithography, which has been reported, for example, for hydrogenated Si(001). In principle, a combination of the controlled desorption and hopping of atomic oxygen can be employed to design the local electronic property on graphene with atomic-scale precision, which may lead to advanced atomic-scale devices based on graphene.

2:40pm **SP+AS+MI+NS+SS-TuA2 Revealing Distance-Dependence of Chemical Interactions and Image Contrast Reversal in Noncontact Atomic Force Microscopy: A Case Study on Highly Oriented Pyrolytic Graphite**, *O.E. Dagdeviren**, *J. Goetzen, E.I. Altman,* ***UdoD. Schwarz***, Yale University

The structural and chemical nature of surfaces governs a material's ability to interact with its surrounding. Designing nanodevices requires tailoring surfaces to meet specific needs and revealing underlying fundamental principles, which determine surface reactivity at the atomic scale. A particularly interesting case occurs when the surface site exhibits varying attraction with distance. To shed light on this issue, noncontact atomic force microscopy experiments combined with scanning tunneling microscopy experiments have been carried out where the evolution of the atom-specific chemical interaction leads to contrast reversal in the force channel. Due to the importance of sp^2-hybridized carbon surfaces in functional nanostructures, we have used highly ordered pyrolytic graphite surface and metal probe tips as the model system. Our experiments reveal that at larger tip-sample distances, carbon atoms exhibit stronger attractions at hollow sites while upon further approach, hollow sites become energetically more favorable [1,2]. The analysis suggests the fundamental factors promoting contrast reversal are local varying decay lengths and an onset of repulsive forces that occurs for distinct surface sites at different tip-sample separations. In addition to these, a change of the hybridization state of carbon atoms from sp^2 to sp^3 under the influence of an approaching reactive probe can also result in contrast reversal. Our experiments address the unexpected nature of contrast reversal due to different governing mechanisms, which are determined by local properties of the sample as well as interacting materials. Combined with in-depth computational analysis, such experiments will lead to a deeper understanding of the fundamental effects that govern how materials interact with their surroundings at sub-nanometer scale. Entangling these fundamental principles with design will enable fabrication and synthesis of better nanodevices with graphene and other layered materials as well as nanotubes.

$^+$ Author for correspondence: omur.dagdeviren@yale.edu

[1] O.E. Dagdeviren et al, Nanotechnology 27, 065703 (2016)

[2] O.E. Dagdeviren et al, Nanotechnology, 27, 485708 (2016)

3:00pm **SP+AS+MI+NS+SS-TuA3 Absence of a Band Gap at Metal-Monolayer MoS$_2$ Interface**, ***Abhay Pasupathy***, Columbia University **INVITED**

Abstract: High quality electrical contact to semiconducting transition metal dichalcogenides (TMDCs) such as MoS$_2$ is key to unlocking their unique electronic and optoelectronic properties for fundamental research and device applications. Despite extensive experimental and theoretical efforts reliable ohmic contact to doped TMDCs remains elusive and would benefit from a better understanding of the underlying physics of the metal-TMDC interface. Here we present measurements of the atomic-scale energy band diagram of junctions between various metals and heavily doped monolayer MoS$_2$ using ultra-high vacuum scanning tunneling microscopy (UHV-STM). Our measurements reveal that the electronic properties of these junctions are dominated by 2D metal induced gap states (MIGS). These MIGS are characterized by a spatially growing measured gap in the local density of states (L-DOS) of the MoS$_2$ within 2 nm of the metal-semiconductor interface. Their decay lengths extend from a minimum of ~0.55 nm near mid gap to as long as 2 nm near the band edges and are nearly identical for Au, Pd and graphite contacts, indicating that it is a universal property of the monolayer semiconductor. Our findings indicate that even in heavily doped semiconductors, the presence of MIGS sets the ultimate limit for electrical contact

4:20pm **SP+AS+MI+NS+SS-TuA7 Imaging of MOS Interface Trap Distribution using Local Deep Level Transient Spectroscopy Based on Scanning Nonlinear Dielectric Microscopy**, *N. Chinone,* ***Yasuo Cho***, Tohoku University, Japan

Physical properties of metal-oxide-semiconductor (MOS) interface are critical for semiconductor devices. There are several techniques for characterizing MOS interface properties. Deep level transient spectroscopy (DLTS)is one of powerful techniques capable of macroscopic quantitative evaluation of trap density at/near MOS interface (D_{it}). But it is easily imagined that actual trap is not homogeneously distributed, but has two dimensional distributions in atomic scale and even in mesoscopic scale. Therefore, it is very important to characterize MOS interface microscopically. Unfortunately, it is impossible to observe such inhomogeneity by using conventional macroscopic DLTS method.

In this paper, a new technique for local DLTS imaging based on scanning nonlinear dielectric microscopy (SNDM) is proposed. This method enables us to observe two dimensional distribution of trap density at/near MOS interface and is demonstrated with oxidized SiC wafer.

45-nm-thick thermal oxide layers were formed on three Si-faces of 4°-off n-type 4H-SiC wafers. One of them was labeled as #S-45-1. The other two wafers were subjected to post-oxidation annealing (POA) in nitric oxide (NO) at different conditions as follows: 1250°C for 10 minutes (#S-45-2), 1150°C for 60 minutes (#S-45-3). The average D_{it} values of these samples were measured by conventional High-Low method, which showed that the D_{it} of #S-45-1 was highest and that of #S-45-3 was lowest.

These three samples were scanned on 1.5x1.5μm^2 square area with a resolution of 30x30 pixels and analyzed using the proposed local DLTS method.

By analyzing the acquired images, time-constant τ and magnitude of transient capacitance response were obtained at each pixel. Highest brightness was obtained from #S-45-1 and lowest one was obtained from #S-45-3, which is consistent with macroscopically obtained result. Furthermore, in the local DLTS images, we detected dark and bright areas, which can be translated as two dimensional trap distribution.

Next, quantitative imaging of D_{it} was performed. Distributions of D_{it} for $\tau = 0.3$ μs and 3 μs were imaged for all samples. The time constants 0.3 μs and 3 μs correspond to energy depth of 0.24 eV and 0.30 eV below the conduction band, respectively. All images have dark and bright areas with feature size of a few 100 nm. In addition, the images with different time constant showed different distribution, which implies that the distribution of interface traps depends on time constant, or suggests the physical origin of interface trap with different energy level is different.

This local DLTS technique can contribute to understanding microscopic physical properties of MOS interface.

4:40pm **SP+AS+MI+NS+SS-TuA8 Quantum State Readout of Individual Quantum Dots by Electrostatic Force Detection**, ***Yoichi Miyahara***, *A. Roy-Gobeil, P.H. Grutter*, McGill University, Canada

Electric charge detection by atomic force microscopy (AFM) with single-electron resolution (e-EFM) is a promising way to investigate the electronic level structure of individual quantum dots (QD). The mechanical oscillation of the AFM tip modulates the energy of the QDs, causing single electrons to tunnel back and forth between QDs and an electrode. The resulting oscillating electrostatic force changes the resonant frequency and damping of the AFM cantilever, enabling electrometry with a single-electron sensitivity. While quantitative electronic level spectroscopy is possible by sweeping the bias voltage, charge stability diagram of the QD can be obtained by scanning the AFM tip around the QD. e-EFM technique can be applied for the investigation of individual colloidal nanoparticles and self-assembled QDs without defining nanoscale electrodes. e-EFM is a quantum electromechanical system where the back-action of a tunneling electron is detected by AFM and can also be regarded as a mechanical analog of admittance spectroscopy with a radio frequency resonator, which is emerging as a promising tool for quantum state readout for quantum information processing. In combination with the topography imaging capability of the AFM, e-EFM is a powerful tool for investigating nanoscale material systems which can be used as quantum bits such as nanowires and single molecules and dopants.

1 Y. Miyahara, A. Roy-Gobeil and P. Grutter, Nanotechnology 28, 064001 (2017).

5:00pm **SP+AS+MI+NS+SS-TuA9 Cryogenic Near-field Imaging and Spectroscopy at the 10-Nanometer-scale**, ***Max Eisele***, *A. Huber*, neaspec GmbH

Near-field microscopy and spectroscopy has become one of the key technologies for modern optics, combining the resolving power of AFM based measurements with the analytical aspects of optical microscopy and spectroscopy. Near-field microscopy has already proven itself vital for modern nanomaterials and has been used in applications such as chemical identification [1], free-carrier profiling [2], or the direct mapping of propagating plasmons [3,4], phonon [5], and exciton polaritons [6]. Key information like the local conductivity, intrinsic electron-doping, absorption, or the complex-valued refractive index can routinely be extracted from these measurements with a spatial resolution of down to 10 nanometer.

*** NSTD Student Award Finalist**

In combination with femtosecond light sources, near-field microscopy has also enabled ultrafast pump-probe experiments [7] with a combined 10-femtosecond temporal and 10-nanometer spatial resolution [8]. Carrier-relaxation dynamics in black phosphorus [9] or graphene [10] are just two examples of the broad range of potential applications for ultrafast near-field nano-spectroscopy.

Within this talk we will introduce the newest technological breakthrough in the field of near-field optics - Cryogenic near-field imaging and spectroscopy. This novel approach has been pioneered by the group of Dimitri Basov at Columbia University and UC San Diego using a home-build cryogenic near-field microscope with a temperature range of 24 – 300 Kelvin. For the first time, this microscope has been capable to spatially resolve the insulator-to-metal phase transition of V2O3 with <25nm spatial resolution [11]. Extending ambient near-field measurements to cryogenic temperatures will open a complete new world for nanoscale optical microscopy and spectroscopy, enabling the direct mapping of phase-transitions in strongly correlated materials or the detection of low-energy elementary excitations at the surface of solid-state systems. A first commercial cryogenic system with a temperature range down to 10 Kelvin is now available from neaspec [12] making this technology broadly available to the community.

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5:20pm **SP+AS+MI+NS+SS-TuA10 Atomic Scale Proximity Effect at a Molecular Superconductor-Metal Boundary**, ***KyawZin Latt***, *S. Khan*, Ohio University, *A. Ngo*, Argonne National Laboratory, *H. Chang*, Ohio University, *A. Hassanien*, J. Stefan Inst., Slovenia, *L. Curtiss*, Argonne National Laboratory, *S.W. Hla*, Ohio University and Argonne National Laboratory

How a superconductor interacts with metal at a superconductor-metal boundary is vital for fundamental understanding of important phenomena such as Andreev reflection, and proximity effect. Here we investigate how the cooper pairs from a charged transfer based molecular superconducting cluster interact with 2-D surface state electrons from Ag(111) surface at the atomic scale using tunneling microscopy, tunneling spectroscopy, and atomic/molecular manipulation schemes at low temperatures in an ultrahigh vacuum environment. The superconducting molecular clusters here are composed of a few molecular chains formed by BETS (donors) and GaCl4 (acceptor). In STM images, these molecular clusters appear as ordered parallel chains resembling the ‘rafts’. Using scanning tunneling microscope (STM) manipulation, small molecular clusters are repositioned on the surface at desired locations. From the tip height signals, the dynamics of molecular clusters during their movements across the surface has been unveiled. Repeated manipulation experiments reveal that the rafts move only along [211] surface directions with single atomic site hops. Tunneling spectroscopy measurements across metal superconductor boundary provides variation of electron structures highlighting how surface state electrons interact with the superconducting clusters.

5:40pm **SP+AS+MI+NS+SS-TuA11 Breaking the Time Barrier in Scanning Probe Force Microscopy: Fast Free Force Reconstruction (F^3R) for Non-contact SPM**, *L. Collins*, ***Stephen Jesse***, *S.V. Kalinin*, Oak Ridge National Laboratory

In the past 3 decades since its invention, the atomic force microscope (AFM) has offered unparalleled insight into both nanoscale structure and surface functionality. At the same time, the spatial resolution afforded by AFM tip is counterpoised by the slow detection speeds compared to other common microscopy techniques (e.g. optical, scanning electron microscopy etc.). This ultimately limits AFM and related measurements to static or quasi-static processes.

In this presentation, we outline a novel time resolved AFM imaging approach, referred to as Fast free force recovery (F^3R)[1] utilizing big data capture and analytics. F^3R-AFM is based on the G-mode acquisition platform [2] and allows direct reconstruction of the tip-sample forces with much higher time resolution (~µs) than possible using standard AFM detection methods (~ms). We describe how fast data acquisition, coupled with multivariate statistical denoising methods can be harnessed to overcome the widely viewed temporal bottleneck in AFM, the mechanical bandwidth of the cantilever. Finally, we will demonstrate quantitative recovery of tip-sample forces with <10 µs time resolution, free from influences of the cantilever ring-down as well as discussing the fundamentally time and information limits of the approach.

[1] Collins, Liam, Mahshid Ahmadi, Ting Wu, Bin Hu, Sergei V. Kalinin, and Stephen Jesse. "Breaking the Time Barrier in Kelvin Probe Force Microscopy: Fast Free Force Reconstruction Using the G-Mode Platform." *ACS nano* (2017).

[2] Belianinov, Alexei, Sergei V. Kalinin, and Stephen Jesse. "Complete information acquisition in dynamic force microscopy." *Nature communications* 6 (2015).

6:00pm **SP+AS+MI+NS+SS-TuA12 Ultrafast G Mode-Kelvin Probe Force Microscopy and its application to probing ionic transport mechanisms in perovskite solar cells.**, ***Liam Collins***, *S. Jesse*, *S.V. Kalinin*, Oak Ridge National Laboratory

Kelvin probe force microscopy (KPFM) is crucial technique for the joint investigations of structural, electronic, and electrochemical functionality on materials ranging from ferroelectrics, and photovoltaics, to battery and fuel cell devices. While KPFM has shown extraordinary success for quantification of equilibrium *or quasistatic* functionalities, this level of information is not sufficient for describing electroactive materials or devices involving fast (< ms) relaxation processes. Practically, the detection methodologies adopted in classical KPFM limit the temporal resolution of the measurement (e.g. ~1-10 MHz photodetector stream is down sampled to a single readout of surface potential per pixel).

In this presentation General Acquisition mode (G-Mode) KPFM[1-3] will be introduced. It will be shown that by harnessing big data acquisition and analytics, it is possible to extract dynamic information on the local electrochemical processes with nanometer spatial and microsecond time resolution. Furthermore, the G-Mode KPFM approach is immediately implementable on all AFM platform, allows capture of numerous channels of information simultaneously (*e.g.* capacitive and potential channels), as well as providing increased flexibility in terms of data exploration across frequency, time, space, and noise domains.

Finally we harness these imaging capabilities to explore non-linear ionic transport in organic-inorganic halide perovskites. We will present imaging of spatio-temporal charge dynamics at the perovskite/electrode interface with <20 µs time resolution and ~10s nm spatial resolution. As will be outlined, based on our observations, we determine that the transport behavior of these materials is considerably more complex than previously argued.

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Applied Surface Science Division
Room: 13 - Session AS+BI+MI+NS+SA+SS-WeM

Beyond Traditional Surface Analysis: Pushing the Limits
Moderators: Svitlana Pylypenko, Colorado School of Mines, Paul Vlasak, The Dow Chemical Company

8:00am **AS+BI+MI+NS+SA+SS-WeM1 Photolysis of Pyruvic Acid in Aqueous Solution as a Source of Aqueous Secondary Organic Aerosol**, ***Yao Fu***, *X.F. Yu*, *F. Zhang*, *Z.H. Zhu*, Pacific Northwest National Laboratory, *J.M. Chen*, Fudan University, *X.Y. Yu*, Pacific Northwest National Laboratory

Pyruvic acid are found in fogs, aerosols and clouds. The sunlight driven reaction pathways of pyruvic acid in the aqueous phase are more elusive compared to its well-known gas phase chemistry. Aqueous solutions containing pyruvic acid in a microchannel after different UV photolysis times up to 8 hours have been studied by in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) for the first time. Both positive and negative ion mode mass spectra provided complementary information of the photochemical aging products at the solution surface. Compared with previous results using bulk approaches (i.e., NMR, ESI-MS), our unique liquid surface molecular imaging enables the observation of photochemical products of pyruvic acid at the aqueous solution surface including oxidation products (i.e., acetic acid, oxalic acid, formic acid, lactic acid), oligomers (i.e., dimethyltartaric acid), and water clusters (i.e., $(H_2O)_nH^+$, $(H_2O)_nOH^-$) with submicrometer spatial resolution. Spectral principal component analysis is used to determine similarities and differences among various photochemical aging samples. SIMS three-dimensional chemical mapping permits visualization of the surface mixing state at the molecular level. For example, oligomers and oxidation products become more significant shown in the chemical spatial mapping with increased photolysis time. In situ molecular imaging of the pyruvic acid aqueous solution surface provides new understanding of complex photochemical reactions as an important source of aqueous secondary organic aerosol (SOA) formation in atmospheric chemistry.

8:20am **AS+BI+MI+NS+SA+SS-WeM2 XPS Depth Profiling of $SrTiO_3$ and HfO_2 with Small Argon Clusters**, ***Christopher Deeks***, Thermo Fisher Scientific, UK, *M. Baker*, University of Surrey, UK, *P. Mack*, Thermo Fisher Scientific, UK

Metal oxides are employed in a wide variety of functional applications. There is currently strong technological interest in strontium titanate ($SrTiO_3$) and hafnium oxide (HfO_2) due to their specific band gaps and high dielectric constants. $SrTiO_3$ is being studied for use in photocatalysis, energy storage and electronic sensors, whilst HfO_2 is widely employed for optical coatings and optoelectronic device applications. Both materials are regularly deposited as thin films and doped to optimise their properties for the application. An accurate determination of thin film composition is paramount to the understanding and optimisation of device performance.

In this work, thin films of $SrTiO_3$ and HfO_2 have been deposited onto silicon substrates and XPS depth profiles have been performed through the thin films using both monatomic and cluster argon ion bombardment. The monatomic Ar^+ profiles were performed using an incident ion energy of 500 eV and the gas cluster ion beam (MAGCIS) profiles were recorded using8 keV Ar_{1000}^+ and 8 keV Ar_{150}^+ for $SrTiO_3$ and HfO_2 respectively. For HfO_2 the optimum results were found when the MAGCIS ion beam was incident upon the sample at a glancing angle. These MAGCIS conditions yielded excellent retention of the original $SrTiO_3$ and HfO_2 stoichiometry during the profile, with no evidence of preferential sputtering or ion beam induced reduction. Using 500 eV Ar^+,however, resulted in the preferential sputtering of oxygen leading to the presence of sub-oxide states in the XPS spectra of Ti in $SrTiO_3$ and Hf and HfO_2. The depth resolution was similar between the monatomic and cluster ion depth profiles for both thin film materials. Using the same incident ion beam angle, the etch rate for 8 keV Ar_{1000}^+ was only 2.5 times lower than that for 500 eV Ar^+. The results will be discussed in the light of known ion beam effects when sputtering metal oxide materials.

8:40am **AS+BI+MI+NS+SA+SS-WeM3 Surface Analysis of Intact Biomolecules: the Bigger They Are the Harder They Fly**, ***Nina Ogrinc Potocnik***, *R. Heeren*, Maastricht University, The Netherlands **INVITED**

Secondary ion mass spectrometry (SIMS), as the oldest MSI techniques, gained popularity for analysis of biological samples due to its ability to obtain chemical and spatial information at unmatched lateral resolutions. The use of focused ion beams for desorption and ionization of surface molecules in SIMS affords for this notable spatial resolution over, for example, laser-based MS approaches such as Matrix Assisted Laser Desorption Ionisation (MALDI). However, the excessive energy of the primary ions limits the method to the detection of elements, fragmented molecules and small intact molecular species. This consequently points at the method's major drawback, which is the difficulty to ionize and detect larger, intact molecular species such as peptides and proteins with great sensitivity. Over the last years, SIMS has been pushing the boundaries by redirecting focus into biomedical applications. Tissue sections and cell imaging has become common practice in research labs all over the world. Now, abundant lipids and small peptides can be studied with different sample surface modifications, where the upper most layer of the surface is sputter coated with a thin layer of metal ((MetA) SIMS – metal –assisted SIMS) or covered with the matrix (ME-SIMS). In both cases the sputtering efficiency and the secondary molecular yield have increased. Here, we studied how ME-SIMS can influence the ionization efficiency of desorbed intact molecules in comparison to MALDI.

First, we imaged mammalian tissue sections that were subjected to a variety of different matrices using a home-built sublimation chamber. Matrix sublimation produces small, homogenous crystal sizes, without the need for solvents that delocalize molecular species. The same or consecutive sections were subsequently analyzed by FTICR-SIMS, to accurately identify the enhanced molecular species of interest specifically intact lipids and metabolites, and by the PHI nano-TOF II for high lateral resolution images and confident identification of said species with tandem MS.Second, *de-novo* peptide sequencing was performed on endogenous neuropeptides directly from a pituitary gland. Careful sample preparation and the capability of using a 1 Da mass isolation window of the precursor ion followed by a collision-induced dissociation (CID) at 1.5 keV in an activation cell with argon gas enables the molecules to be fragmented in a specific pattern. Neuropeptides up to *m/z* 2000 were detected and sequenced from the posterior lobe. Further on, we applied it for the characterization of tryptically digested peptides from a variety of tissue sections investigating the applicability to bottom-up proteomics.

9:20am **AS+BI+MI+NS+SA+SS-WeM5 Hydrogen/Deuterium Exchange Using Vapor Phase D_2O to Enhance SIMS Characterizations**, ***Paul Vlasak***, The Dow Chemical Company

Hydrogen/Deuterium exchange of labile hydrogens is a well-known water solution-based phenomenon that has in recent years seen extensive use in the area of protein characterization. This presentation will demonstrate a method to accomplish vapor phase hydrogen/deuterium exchange of solid sample surfaces prior to analysis by SIMS. In many cases, it is not desirable to expose the sample to liquid solvent due to the possibility of dissolving and rearranging or removing surface species of interest. In contrast, the effect of vapor phase D_2O exposure is similar to typical exposures of the sample to humid room air.

The described method is simple and inexpensive in comparison with synthetic isotopic labeling studies. However, it is expected that only the sufficiently labile and sterically accessible H atoms can be tagged, typically those bound to N, O, or S. Possible benefits of this method include isomer differentiation, elucidation of fragmentation pathways, fundamental studies of ionization, differentiation of sterically or otherwise protected vs. unprotected functional groups, and determination of water diffusion or permeability in solid materials.

9:40am **AS+BI+MI+NS+SA+SS-WeM6 Fragmentation and Backscattering of Large Ar_n^+ Clusters as a Probe of Polymer Glass Transition**, *C. Poleunis*, Université Catholique de Louvain, Belgium, *V. Cristaudo*, Université Catholique de Louvain, Belguim, ***Arnaud Delcorte***, Université Catholique de Louvain, Belgium

Gas cluster ion beams (GCIB) have become the standard sources for molecular depth-profiling of organic materials with secondary ion mass spectrometry (SIMS) [1] and X-ray photoelectron spectroscopy (XPS). Since 2009, a number of experimental and theoretical studies were devoted to the investigation of the effects of energy, nuclearity and incidence angle of the Ar clusters on the energy deposition, fragmentation and molecular emission induced in organic solids [2-4]. Recently, Mochiji et al. reported that the backscattered Ar_n^+ clusters observed in the SIMS spectra of pure metal surfaces provide information on the mechanical properties of the surfaces analysed by GCIB [5]. They correlated the ratio of Ar_2^+ to the sum of Ar_n^+ clusters intensities with the impulsive stress caused by the impact, a parameter directly linked to the elastic modulus of the material.

Here, the intensity variations of the backscattered Ar_n^+ clusters are studied as a function of temperature for a series of thermoplastic polymers: high molecular weight polydisperse polyisobutylene and polybutadiene, polystyrene (Standard; $M_w = 4000$) and polymethyl methacrylate (Standards; $M_w = 2000$ and 150000). For all these polymers, our results show a transition of the intensity ratio $Ar_2^+/(Ar_2^++Ar_3^+)$ when the temperature is scanned from

-120 °C to +125 °C. This transition generally spans over a few tens of degrees and the temperature of the inflexion point of each curve is very close to the glass transition temperature (T_g) reported for the considered polymer. Due to the surface sensitivity of the cluster backscattering process (a few nanometers as indicated by molecular dynamics simulations [4]), the presented analysis could provide a new method to specifically evaluate the surface T_g of polymers, with the same lateral resolution as the gas cluster beam. The results are discussed from the point of view of the structure and mechanics of polymers.

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11:00am AS+BI+MI+NS+SA+SS-WeM10 Evolution of the Bi Cluster LMIS as a Universal Source for High Performance SIMS Analysis

*Felix Kollmer**, ION-TOF GmbH, Germany **INVITED**

In 1987 Appelhans and co-workers performed a groundbreaking experiment. They bombarded a polymer surface with a neutral SF6 beam in order to avoid charging effects on insulators. By coincidence they discovered that "the SF_6 beam is doing an excellent job of producing secondary ions ... it is unexpectedly efficient at sputtering secondary ions from these polymer surfaces "[1].

In the following years the bombardment of organic surfaces with clusters was investigated by many research groups. The lateral resolution of the applied beams was rather low since the focus at this time was clearly on the fundamentals of the ion solid interaction and the secondary ion generation. However, as early as 1991 Benguerba applied an Au cluster liquid metal ion source (LMIS) for a fundamental study of phenylalanine [2].

At the beginning of the millennium Au cluster LMIS became commercially available for TOF-SIMS instrumentation. This led to a wider application in the SIMS community and to a further improved performance. However, the cluster sources remained an additional option for the SIMS instruments especially since the low cluster currents did not allow the replacement of the reference Ga LMIS for many applications.

With the introduction of a LMIS operated with Bi this changed fundamentally [3]. Roughly 50% of the beam consists of clusters and 50% are emitted as mono-atomic Bi species. This ensures a large flexibility for the analysis of inorganic as well as organic surfaces. Moreover, an uncompromised performance in terms of lateral and mass resolution is achieved, even with cluster beams, and a lateral resolution in the sub 20 nm range has been demonstrated with Bi_3^{++} species [4].

Today, the Bi LMIS is used as the standard analysis source on more than 250 TOF-SIMS instruments for all kinds of applications. In combination with a massive cluster beam that is applied for the erosion of the sample (e.g. Ar_n) even depth profiling or 3D analysis of organic samples is possible.

In this contribution, we will have a retrospective look at the development of high performancecluster SIMS. Besides fundamental capabilities of the Bi LMIS and the secondary ion generation we will discuss milestones of the application as well.

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11:40am AS+BI+MI+NS+SA+SS-WeM12 Evaluating the Benefits of Cs Cluster Analysis in ToF-SIMS and Cs/Xe Co-sputtering for Depth Profiling Layered Thin Films

James Ohlhausen, *P.T. Vianco, M.T. Brumbach, R. Chow*, Sandia National Laboratories

Depth profiling with Cs to create MCs^+ clusters can produce semi-quantitative results by greatly reducing the matrix effects observed in common M^+ analysis. Additionally, alkali metal clusters enhance negative ion detection in the form of positive Cs clusters, such as MCs^+ and MCs_2^+. In his review article, Wittmaack[1] discussed the many ways that Cs is used in SIMS analyses to provide this enhancement which includes using Cs as the sputtering species and/or analytical probe and using directed Cs vapor. Unfortunately, high Cs surface concentrations can lead to suppression of Cs cluster formation. Xenon and Cs can be co-sputtered in a ToF-SIMS system to adjust the relative amounts of Cs and Xe in the co-sputtered beam to control Cs surface concentration and optimize Cs cluster formation[2]. Cs/Xe co-sputtered depth profiling has been shown to work well in materials systems such as Au thin film on Si[3] and Pd-Rh thin film[4].

The present paper discusses the use of Cs/Xe co-sputtering to investigate an Au/Pd/Ni electroplated layered system. Gold and to some extent Pd have low positive ionization yields, so typical ToF-SIMS data from these metals can be difficult to interpret. However, Cs/Xe co-sputtering has been found to generate high yield MCs^+ clusters in Au and Pd, thus enabling this analysis. This Au/Pd/Ni metal stack were analyzed in a pristine (as received) condition, after accelerated aging and after exposure to a (very high temperature) solder reflow process. The elemental and molecular sensitivities as well as quantitative results stemming from this analysis will be investigated. The manner whereby these results support the use of Au/Pd/Ni stack in an engineering application will be shown. In particular, interlayer diffusion, trace contaminants and interfacial contamination will be examined. Comparisons will be made to Auger and XRF to assess quantitation and sensitivity and to illustrate the advantage of this SIMS technique.

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12:00pm AS+BI+MI+NS+SA+SS-WeM13 Real-Time Monitoring Electrochemical Reaction Intermediates using *In Situ* Time-of-Flight Secondary Ion Mass Spectrometry

Jun-Gang Wang, East China University of Science and Technology; Pacific Northwest National Laboratory (PNNL), *Y. Zhang, X.Y. Yu, Z.H. Zhu*, PNNL

In situ monitoring of electrochemical reactions is traditionally performed by cyclic voltammetry[1], plasmonic spectroelectrochemistry[2, 3], and surface probing techniques such as scanning electrochemical microscopy and scanning ion conductive microscope.[4] However, it has been extremely difficult to obtain direct molecular evidence of the electrochemical reaction intermediates using these traditional techniques. Thus, the debate of rection machnisms has long been an issue. Recently, mass spectrometric techniques have been coupled with electrochemistry to provide the molecular information of intermediates of redox reactions.[5] The advantage of mass spctetrometric techniques is that capture of molecular ions can provide direct molecular information of key chemical species, such as rection intermediates. A novel approach, based on coupling of time-of-flight secondary ion mass spectrometry (ToF-SIMS) and electrochemistry has been developed in Pacific Northwest National Laboratory and it has been used for in situ analysis of reaction intermediates in electro-oxidation of ascorbic acid at the electrode–electrolyte interface.[6] Herein, the electrochemical oxidation of acetaminophen was chosen as a model system, which simulated the function of oxidase enzymes cytochrome P-450 to catalyze the oxidation of acetaminophen.[7] This reaction was real-time monitored using in situ ToF-SIMS. The highly reactive N-acetyl-p-benzoquinone-imine (NAPQI) was captured. The NAPQI subsequently conjuated with glutathione and cysteine was molecularly confirmed. We demonstrated the proof of principle for the use of ToF-SIMS for real-time monitoring of electrochemical reaction with high chemical specificity. Our results demonstrate that the coupling of ToF-SIMS and electrochemistry has great potential to molecularly elucidate reaction machnisms in the oxidative metabolism, pharmaceutical intoxification, and cell toxicology.

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* **ASSD Peter Sherwood Award**

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Magnetic Interfaces and Nanostructures Division
Room: 11 - Session MI+SA-WeM

Controlling Magnetism in Oxides and Multiferroics and Chirality in Spin Transport and Magnetism (cont.)
Moderator: Valeria Lauter, Oak Ridge National Laboratory

8:20am **MI+SA-WeM2 Integrated Magnetics and Multiferroics for Compact and Power Efficient Sensing, Power, RF, Microwave and mm-Wave Tunable Electronics**, ***Nian Sun***, Northeastern University **INVITED**

The coexistence of electric polarization and magnetization in multiferroic materials provides great opportunities for realizing magnetoelectric coupling, including electric field control of magnetism, or vice versa, through a strain mediated magnetoelectric coupling in layered magnetic/ferroelectric multiferroic heterostructures [1-9]. Strong magnetoelectric coupling has been the enabling factor for different multiferroic devices, which however has been elusive, particularly at RF/microwave frequencies. In this presentation, I will cover the most recent progress on new integrated multiferroic materials and devices for sensing, and from power to mm-wave electronics. Specifically, we will introduce magnetoelectric multiferroic materials, and their applications in different devices, including: (1) ultra-sensitive magnetometers based on RF NEMS magnetoelectric sensors with picoTesla sensitivity for DC and AC magnetic fields, which are the best room temperature nano-scale magnetometers; (2) novel ultra-compact multiferroic antennas immune from ground plane effect with f200µm × 1µm or l_0/600 in size, -18dBi gain, self-biased operation and 1~2% voltage tunable operation frequency; and (3) novel GHz magnetic and multiferroic inductors with a wide operation frequency range of 0.3~3GHz, and a high quality factor of close to 20, and a voltage tunable inductance of 50%~150%. At the same time, I will also demonstrate other voltage tunable multiferroic devices, including tunable isolating bandpass filters, tunable bandstop filters, tunable phase shifters, etc. These novel integrated multiferroic devices show great promise for applications in compact, lightweight and power efficient sensing, power, RF, microwave and mm-wave integrated electronics.

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9:20am **MI+SA-WeM5 Controlling Spin Selectivity in Photoinduced Charge Transfer through Patterned DNA Microarrays**, ***John Abendroth****, *N. Nakatsuka, M. Ye, D. Stemer,* University of California at Los Angeles, *D. Kim, E. Fullerton,* University of California at San Diego, *A. Andrews, P. Weiss,* University of California at Los Angeles

Understanding spin-selective interactions between electrons and chiral molecules is critical to elucidating the prospective significance of electron spin in biological processes. We report the visualization of spin-dependent charge transport in microscale-patterned, self-assembled monolayers of double-stranded DNA on ferromagnetic substrates using fluorescence microscopy. Patterned DNA arrays provide background regions in every measurement to quantify the substrate magnetization-dependent fluorescence due to the chiral-induced spin selectivity effect. Fluorescence quenching of photoexcited dye molecules bound within DNA duplexes is dependent upon the rate of charge separation/recombination upon photoexcitation and efficiency of DNA-mediated charge transfer to the surface. Here, the latter process is modulated with an external magnetic field to switch the magnetization orientation of the underlying ferromagnetic substrates. Using this experimental technique, we are investigating molecular parameters that can be manipulated to influence the *magnitude* of the spin selectivity effect in DNA arrays to assess candidly the potential of chiral assemblies for organic spintronics. In particular, we are monitoring the influence of heavy metal species that are incorporated predictably within DNA duplexes to change the strength of molecular spin-orbit coupling as a result of the heavy atom effect.

9:40am **MI+SA-WeM6 Anomaly in Electric Transport Behaviour of Fe_3O_4 Thin Films**, ***Murtaza Bohra***, Mahindra Ecole Centrale, India

Nanocrystalline Fe_3O_4 thin films were grown by adopting two different reduction approaches (1) vacuum annealing (2) wet H_2 annealing . While vacuum annealed films shows Verwey transition with lower resistivity compared to the bulk Fe_3O_4, the same are not observed in electric transport properties of wet H_2 annealed films. However, this transition was clearly seen in the temperature dependence of magnetization of both sets of Fe_3O_4 thin films. This seems to indicate that the both electric transport and magnetization are independent processes; it's just coincidence to happen at same place of Verwey transition at 120 K in Fe_3O_4. Different electric transport properties in both reductions treated Fe_3O_4 films could be ascribed to different grain sizes/grain boundary volumes, inhomogeneities and presence of residual atomic-H at grain boundaries emanating from complex reductions treatments.

11:00am **MI+SA-WeM10 Intrinsic Interfacial Phenomena and Spin Structure in Nano and Heterostructures**, ***Carlos Vaz***, Paul Scherrer Institut, Switzerland **INVITED**

One fundamental route towards the control of the electronic properties of materials is via modulation of the charge carrier density, either through chemical, ionic, or electrostatic doping. The latter process relies on charge screening effects at the interface between a gate dielectric and a channel layer, and forms the basis of important technological applications, such as field effect devices. A more recent extension of this concept employs a ferroelectric gate dielectric in combination with correlated materials to form switchable, non-volatile ferroelectric field effect devices, or artificial multiferroic heterostructures relying on interfacial modulations of the magnetic properties of the channel layer [1]. A particularly striking manifestation of the latter has been found in ferroelectric/ferromagnetic mixed valency manganite heterostructures, where control of the ground state of a 10 unit cells La0.8Sr0.2MnO3 film (LSMO) in contact with a ferroelectric PZT layer leads to a spin reconstruction in the LSMO that is intrinsic to the PZT/LSMO interface, as a consequence of the modulation in the charge density [2]. In this contribution I discuss recent results aiming at resolving the magnetic configuration of the interfacial spin reconstruction in the LSMO using soft x-rays as a localised probe of the electronic and magnetic structure at the interface. In particular, I show that resonant x-ray magnetic reflectivity can probe deeply buried interfaces with high sensitivity. Changes in the reflectivity spectra are observed upon switching of the ferroelectric polarisation and reflect directly the changes in the spin structure at the interface. The results of these studies underline the unique strengths of synchrotron x-ray light to address fundamental and practical issues in a wide range of physical systems [3].

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11:40am **MI+SA-WeM12 Enantiomer-dependent Spin Orientation in Photoelectron Transmission through Heptahelicene Molecules**, ***Matthias Kettner***, *D. Nürenberg,* University of Münster, Germany, *J. Seibel,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, *H. Zacharias,* University of Münster, Germany, *K.-H. Ernst*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The interaction of electrons with helical molecules attains growing interest due to a spin selectivity in electron transmission. Experiments on self-assembled monolayers of double stranded DNA [1] and oligopeptides [2,3] indicated a very efficient spin filtering behavior of the molecules at room temperature.

In present experiments enantiopure M- and P-heptahelicene molecules are evaporated onto different metal single crystal surfaces. The molecules arrange themselves to a highly ordered monolayer [4,5]. Samples are then irradiated with $\lambda = 213$nm laser radiation to generate photoelectrons from the substrate. These electrons are transmitted through the heptahelicene layer and analyzed with regard to their average longitudinal spin orientation by Mott scattering. The sign of the spin polarization depends on the helicity of the enantiomer. The effect of the heptahelicene on the spin orientation seems to be independent on the substrate.

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12:00pm **MI+SA-WeM13 Spin-selective Electron Transmission through Self-Assembled Layers of PNA**, ***Paul Möllers***, *M. Kettner, D. Nürenberg,* Westfälische Wilhelms-Universität Münster, Germany, *F. Tassinari, T. Markus,* Weizmann Institute of Science, Israel, *C. Achim,* Carnegie Mellon University, *R. Naaman,* Weizmann Institute of Science, Israel, *H. Zacharias,* Westfälische Wilhelms-Universität Münster, Germany

The yield of electrons transmitted through chiral molecules can depend on the electron's spin; chiral molecules can therefore act a spin filters. This effect is referred to as chirality-induced spin selectivity (CISS). Previous experiments have e.g. been performed with monolayers of double-stranded DNA adsorbed on gold [1] and silicon [2] substrates. In this contribution, we present results of our spin-resolved photoemission experiments performed at room temperature. The samples consist of self-assembled monolayers of helical molecules – various types of double-stranded peptide nucleic acid (PNA) – on polycrystalline gold surfaces. The samples are irradiated by a laser at $\lambda = 213$nm to generate photoelectrons from the gold substrate which are then transmitted through the adsorbed monolayer. Subsequently, the electrons are analyzed by a Mott polarimeter. We found longitudinal spin polarizations of −6% for PNA and +25% for γ-PNA. The results indicate that the adsorbed molecules act as a spin filter.

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Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room: 9 - Session SA+2D+AC+MI-WeM

Recent Advances of Diffracting/Scattering and Spectroscopic Methods for Correlated and 2D Materials

Moderators: Hans-Peter Steinrück, University Erlangen-Nuernberg, Germany, Kristina Edström, Uppsala University, Sweden

8:00am **SA+2D+AC+MI-WeM1 Studies of Surfaces and Catalysis in real time with X-ray Free Electron Laser**, ***Anders Nilsson***, Stockholm University, Sweden **INVITED**

In heterogeneous catalysis, reactants adsorbed on surfaces are converted to products, which eventually desorb via various intermediates. The transition state separates reactants and intermediates from products and the free energy required to reach it determines the kinetics of an elementary chemical reaction. Many surface reaction intermediates are, however, transient species with a short residence time and the population of species in the transition state region is near-zero making their observation a challenge during steady state conditions. Ultrafast pump-probe techniques have, however, opened up opportunities by promoting a sufficient population of molecules in transient states to allow detection on short time scales. Here recent results on probing chemical reactions on surfaces using X-ray free-electron lasers LCLS (Linac Coherent Light Source) at SLAC National Accelerator Laboratory) will be presented. Four examples will be shown CO desorption, Oxygen activation, CO oxidation and CO hydrogenation on Ru(0001). We demonstrate that both transient intermediates and the transition state region can be detected in surface chemical reactions.

8:40am **SA+2D+AC+MI-WeM3 New Generation RIXS of 3*d*-TM Oxides**, ***Giacomo Ghiringhelli***, Politechnico Milano, Italy **INVITED**

Resonant inelastic soft x-ray scattering huge potential is quickly becoming reality. RIXS is element and site selective, like x-ray absorption spectroscopy. It is momentum resolved, like x-ray diffraction. And it probes several kinds of excitations at a time, from charge transfer and electron-hole pair generation, to orbital (*dd* or *ff*) excitations, to spin waves and lattice modes, unlike any other energy loss spectroscopy. Moreover, the elastic component of the spectra carries information on commensurate and incommensurate orders, such as charge density waves (CDW) and orbital order. The ERIXS endstation at the ID32 beam line of the ESRF is the founder of a new generation of RIXS instruments capable of exploiting all the strongpoints of this technique, thanks to the very high resolving power (30,000 at 1 keV), the diffractometer-like manipulator and the full control of photon polarization provided by the combination of the APPLE II source and the polarimeter on the analyzer.

I will review some of the results obtained in the first year of operations of ID32, with a special focus on cuprate superconductors studied at the Cu L_3 edge. High resolution RIXS has been used to determine the relation between crystal structure and the extent of hopping integrals in parent compounds, revealing why apical oxygens are detrimental to superconductivity [1]. Ultra-high resolution RIXS has provided a direct measurement of the momentum-dependent electron phonon coupling in undoped and superconducting samples, and has revealed new collective modes related to charge density waves (CDW) in underdoped Bi2212. Polarization analysis has definitively demonstrated the spin-flip character of the mid-IR spectral region in superconducting compounds. And the quasi-elastic part of RIXS spectra has brought new evidence of the universality of charge ordering phenomena in cuprates, including striped cuprates [2] and single layer Bi2201. Finally the feasibility of high resolution RIXS in standing wave geometry has been successfully demonstrated, adding depth control on this bulk sensitive technique.

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9:20am **SA+2D+AC+MI-WeM5 Resonant Inelastic X-ray Scattering on Low-Dimensional Correlated Transition Metal Oxides and Oxide Heterostructures**, ***Thorsten Schmitt***, Paul Scherrer Institut, Switzerland **INVITED**

Resonant inelastic X-ray scattering (RIXS) is a powerful bulk-sensitive photon-in / photon-out spectroscopic probe of the electronic structure of condensed matter with atomic and orbital sensitivity. It is a unique tool for studying excitations from the electronic ground state in correlated transition-metal oxides, being directly sensitive to lattice-, charge-, orbital- and spin-degrees of freedom. In this talk, we report RIXS investigations of the $LaTiO_3$ layers in $(LaTiO_3)_n/(LaAlO_3)_5$ superlattices undergoing a transition from Ti^{3+} to Ti^{4+} oxidation state upon reducing n and thickness as well as temperature-driven metal-insulator transitions in thin films of $CaVO_3$.

$(LaTiO_3)_n/(LaAlO_3)_5$ superlattices (SL) composed of a band-insulator ($LaAlO_3$) and a Mott-insulator ($LaTiO_3$) present an enhanced insulating character when n is reduced. We prepared a set of SLs (n=10, 5 and 2 unit cells) and investigated these with X-ray absorption spectroscopy (XAS) and RIXS. XAS shows a clear change in the Ti valence going progressively from the nominal Ti^{3+} ($3d^1$, n=10 u.c.) for bulk $LaTiO_3$ to an almost pure Ti^{4+} ($3d^0$, n=2 u.c.). RIXS reveals two spectral developments when reducing the $LaTiO_3$ thickness n: 1) reduction of intra-t_{2g} / intra-e_g splitting and increase of t_{2g} to e_g separation and 2) increase of the charge transfer excitation spectral weight. The changes in the energy of the orbital levels observed as a function of n reveal a clear change of the local TiO_6 distortion. We suggest that an inverse Jahn-Teller effect, inducing the octahedra to assume higher symmetry, is responsible for the observed orbital energy shifts. This peculiar effect is partially caused by strain, triggering a $3d^1 \rightarrow 3d^0$ electron transition at the interfacial Ti sites.

Bulk $CaVO_3$ is a correlated paramagnetic metal. Thin films of $CaVO_3$ undergo a metal-insulator transition (MIT) when the thickness is reduced below ca. 20 u.c.. Our XAS and RIXS measurements at the V L-edge across this dimensionality driven MIT in $CaVO_3$ reveal a large transfer of spectral weight from fluorescent to Raman modes upon entering the insulating state. We observe a large reduction in the charge excitation bandwidth and V-O covalence across the thickness and temperature-driven MIT. Further analysis of the charge modes suggests a bandwidth-controlled MIT, assisted by the presence of strong correlations.

11:00am **SA+2D+AC+MI-WeM10 Doping of Graphene Exploited with Spectromicroscopy**, ***Carla Bittencourt***, University of Mons, Belgium **INVITED**

Limitations in characterisation and theoretical modelling tools have been a major obstacle for the engineering of novel functional materials with properties enhanced by their nanoscale morphology, because detailed understanding of the structure–property–operando relationships are required. In this perspective technology has entered in a period of convergence between theory and characterisation tools, traditional spectroscopic techniques are being combined with microscopy to characterise individual nano-objects. In this context advances in the design and fabrication of x-ray focusing systems allow modifying conventional X-ray spectroscopies using synchrotron light to be used to study individual nanostructures and selected regions of a nanoscale sample. These spectroscopies are amongst the most powerful tools in material science providing elemental, electronic, structural and chemical information. Recent trends include in-operando analysis of individual nanostructures.

In my talk I will report recent results obtained using spectromicroscopy techniques to study the doping of suspended graphene flakes. The nitrogen doping of suspended graphene was performed via ion implantation. We will show that inclusion of up to 20 at.% nitrogen can be reached, while maintaining a sp^2-network. The evolution of nitrogen species: pyridinic, graphitic, and pyrrolic, at different doping stages and annealing temperatures is observed by scanning X-ray photoelectron microscopy (SPEM). Variations in the ratio between sp^2 nitrogen species is observed for increasing treatment time; thermally heating the doped carbon nanostructure results in quenching of the sp^3 component, suggesting the graphitic nitrogen as the most thermal stable species. The effect of the interaction of molecular oxygen with nitrogen doped graphene will be discussed.

11:40am **SA+2D+AC+MI-WeM12 Multi-modal and Multi-dimensional Synchrotron Investigation of Functional Materials**, ***Karen Chen-Wiegart***, Stony Brook University/Brookhaven National Laboratory **INVITED**

Multi-modal and multi-dimensional characterization at synchrotrons can provide unprecedented information for complex, heterogeneous materials system. A multi-modal approach combines multiple synchrotron techniques to gain complementary information. Furthermore, with imaging techniques specifically, multi-dimensional imaging includes techniques such as tomography, spectroscopic microscopy, or in *situ/operando* imaging. These capabilities are particularly powerful when used to study complex structures with morphological and chemical heterogeneity. This talk will address the applications in energy storage and conversion materials, including Li-ion batteries, Li-S batteries, and solid-oxide fuel cells. Other examples, including nano-/meso-porous metals, cultural heritage and surface treatment on metals will also be briefly discussed.

Thin Films Division
Room: 21 - Session TF+EM+MI-WeM

Thin Films for Microelectronics
Moderators: Erwin Kessels, Eindhoven University of Technology, The Netherlands, Adrie Mackus, Eindhoven University of Technology, The Netherlands

8:00am **TF+EM+MI-WeM1 Electrode Modulated Electric Field Capacitance Nonlinearity in ALD Al_2O_3 and HfO_2 Metal-Insulator-Metal Capacitors**, *D.Z. Austin, K. Holden*, ***John Conley, Jr.***, Oregon State University

Back-end-of-line metal-insulator-metal capacitors (MIMCAPs) require increasing capacitance density (C_{ox}) while maintaining low leakage current density (J_{leak}). In addition, analog and mixed signal (AMS) applications are particularly sensitive to nonlinearity of capacitance-voltage (CV), empirically characterized by the quadratic voltage coefficient of capacitance, α_{VCC}. Scaling of MIMCAPs for AMS applications is increasingly challenging as C_{ox}, J_{leak}, and α_{VCC} are all inversely proportional to dielectric thickness (d_{ox}). Despite its technological importance, the fundamental mechanisms responsible for α_{VCC} are not fully understood. It is well established that the "bulk" dielectric material has a dominant effect, where α_{VCC} increases with increasing dielectric constant and roughly as $1/d_{ox}^2$. However, the influence of the electrode interfaces is not currently understood. Of the few studies that have considered the impact of the electrodes on α_{VCC}, most have focused on interfacial layer oxides (ILOs).

In this work, metals with low enthalpy of oxide formation (ΔH_{ox}), are used to examine the influence of the top electrode interface, in the absence of a significant ILO, on the CV nonlinearity of TaN bottom electrode MIMCAPs with various thickness ALD HfO_2 and Al_2O_3. If non-linearity is purely a bulk effect then normalizing for d_{ox}, one would expect that the *electric field* coefficient of capacitance (α_{ECC}) should be independent of d_{ox}. Instead, we find that α_{ECC}*decreases* with decreasing d_{ox}, indicating either an ILO or the direct influence of the interface. A plot of capacitive equivalent thickness vs. optical thickness rules out an ILO. For Au, Ag, Pd, and Ni, α_{ECC} increases with increasing d_{ox}, saturating for thick oxides. It has been proposed that for positive α_{VCC} materials ($C_{ox}(V)$ increases with voltage), electrostriction and Maxwell stress lead to a vertical compression of the oxide under applied fields that results in increased capacitance. We further propose that the oxide must expand horizontally to maintain volume. This expansion results in compressive stress in the oxide and tensile stress in the metal, concentrated near the interface. The electrode then serves to inhibit the lateral expansion of the dielectric, reducing overall α_{ECC}. Indeed α_{ECC} of 10 nm oxides was found to increase roughly linearly with increased oxide/metal % lattice mismatch. As thinner oxides are used to achieve higher C_{ox}, the metal electrodes exert influence over a greater % of the oxide thickness, increasing the electrode importance and its impact on nonlinearity.

New understanding of the impact of electrodes on α_{ECC} should aid in rapid optimization of low α_{ECC} MIMCAPs.

8:20am **TF+EM+MI-WeM2 Difference of the Hysteresis in Capacitance-voltage Characteristics of ALD-Al_2O_3 MIS Capacitors on Si and GaN Substrate**, ***Masaya Saito***, *T. Suwa, A. Teramoto,* Tohoku University, Japan, *T. Narita,* Toyota Central R&D Labs. Inc., Japan, *T. Kachi*, Nagoya University, Japan, *R. Kuroda, S. Sugawa*, Tohoku University, Japan

We evaluated the difference of hysteresis in capacitance-voltage(C-V) characteristics of ALD-Al_2O_3 MIS capacitors for different semiconductors. N-type Cz-Si and n-type GaN wafers which had the bandgap energies of 1.12 and around 3.4 eV, respectively, were used as semiconductor layers for MIS structures. N-type Si wafer was doped with P of 5×10^{14} cm^{-3}. The upper layer (2 µm) of n-type GaN wafer was doped with Si of 5×10^{16} cm^{-3} using a metal-organic vapor phase epitaxy. As the gate insulator layers of the MIS structures, the 10 nm-thick Al_2O_3 films were formed by the Atomic Layer Deposition (ALD) using $Al(CH_3)_3$ and H_2O at 75 ^oC, followed by the formation of aluminum as the gate electrodes. MIS capacitors were irradiated by the light of white LED to only before the voltage sweeps of C-V measurements at -3 V followed by the voltage sweeps of -3 à 3 V and 3 à -3 V without irradiation.

We observed that the clockwise hysteresis in the case of Si gradually decreased as increasing the time of measurement. On the contrary, the hysteresis in the case of GaN was also clockwise and drastically decreased at the second measurement. It is considered that this difference was caused by the difference of bandgap energies between Si and GaN. In the case of Si, some electrons (holes) injected from Si substrate were trapped to the state near the Al_2O_3/Si interface when the positive (negative) bias was applied to gate electrode. When applying the subsequent negative (positive) bias, most of these charges were released because the bandgap energy of Si is small. In the case of GaN, most of these charges trapped to the state near the Al_2O_3/GaN interface were not released within the measurement time because of the interface states far from the both band edges owing to the larger bandgap energy of GaN. Therefore, the different hystereses for their MIS capacitors were probably caused by the difference that the trapped charges to the state in the bandgap were released in the case of Si but not released in the case of GaN.

Acknowledgement:

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8:40am **TF+EM+MI-WeM3 Monolithic Integration of C-type Erbium Oxide on GaN(0001) by Atomic Layer Deposition**, ***Pei-Yu Chen***, *A. Posadas,* The University of Texas at Austin, *S. Kwon, Q. Wang, M. Kim,* The University of Texas at Dallas, *A. Demkov, J.G. Ekerdt*, The University of Texas at Austin

Motivated by the need for faster device speed, the industry is considering compound semiconductors, such as gallium nitride (GaN) in the III-V family of materials, which have higher electron mobility than silicon. To passivate the nitride surfaces and enable GaN-based electronic devices, a high quality and thermally stable dielectric layer material is required. Recently, rare earth sesquioxides have received attention due to their electrical properties, thermal and chemical stability, and relatively high dielectric constant [1]. Using atomic layer deposition (ALD) with erbium tris(isopropylcyclopentadienyl) [$Er(^iPrCp)_3$] and water, crystalline cubic (C-type) Er_2O_3 is successfully grown on GaN at 250 °C for the first time. ALD enables the conformal deposition of Er_2O_3 film on GaN and features a stable growth rate of 0.82 Å/cycle in this work. *In-situ* x-ray photoelectron spectroscopy is used to determine film composition and *in-situ* reflection high-energy electron diffraction is used to verify the surface order and the film crystallinity at various stages in the growth process. The cubic structure of Er_2O_3 is confirmed by a combination of both out-of-plane and in-plane X-ray diffraction (XRD). The orientation relationships between C-Er_2O_3 film and GaN substrate are C-Er_2O_3(222) || GaN(0001), C-Er_2O_3(-440) || GaN(11-20), and C-Er_2O_3(-211) || GaN(1-100). The out-of-plane C-Er_2O_3(222) XRD peak shifts as a function of film thickness indicating a slight change in *d*-spacing caused by the presence of strain at the interface as shown in **Fig. 1(a)(b)**. The observed tensile strain results from the lattice mismatch between GaN and Er_2O_3. As the film thickness increases, the C-Er_2O_3 becomes more relaxed. In-plane XRD also displays peak shifts with opposite trend from the out-of-plane scan as expected. Scanning transmission electron microscopy (STEM) is used to examine the microstructure of C-Er_2O_3 and its interface with GaN and is in excellent agreement with the simulated atomic positions (**Fig. 1(c)**). An interfacial layer consisting of 1-3 atomic-layers is observed by STEM. The electron energy loss spectroscopy (EELS) profiles for Ga, Er, O, and N suggest partial oxidization of GaN at the interface. Overall, this work demonstrates a low temperature, all-chemical process for the growth of crystalline C-Er_2O_3 on GaN by ALD.

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9:00am **TF+EM+MI-WeM4 High-Performance p-Type Thin Film Transistors Using Atomic-Layer-Deposited SnO Films**, *S.H. Kim, I.-H. Baek, J.J. Pyeon,* Korea Institute of Science and Technology, Republic of Korea, *T.-M. Chung, J.H. Han,* Korea Research Institute of Chemical Technology, Republic of Korea, ***SeongKeun Kim***, Korea Institute of Science and Technology, Republic of Korea

Since the report of thin film transistors (TFTs) utilizing an amorphous oxide semiconductor of the In–Ga–Zn–O system exhibiting high electron mobility by the Hosono group, considerable efforts have been dedicated to implement these TFTs for emerging applications including flat-panel and flexible displays. Compared with the great progress and success regarding n-type oxide semiconductors, the current status of the development of p-type oxide semiconductors remains far behind.

SnO is a promising p-type oxide with relatively high hole mobility. The low formation energy of Sn vacancies and the more dispersed VBM resulting from hybridization of oxygen 2p and Sn 5s orbitals allow the p-type conduction of SnO. One critical challenge for high-performance SnO TFTs is the instability of the SnO phase. SnO is less stable than SnO_2, indicating the difficulty of growth of SnO.

Here, we demonstrate high-performance p-type TFTs with a single phase SnO channel layer grown by atomic layer deposition (ALD). The performance of the SnO TFTs relies on hole carriers and defects in SnO and near the back-channel surface of SnO as well as the quality of the gate dielectric/SnO interface. The growth of SnO films at a high temperature of 210 °C effectively suppresses the hole carrier concentration, leading to a high on-current/off-current (I_{on}/I_{off}) ratio. In addition, the SnO films grown at 210 °C achieve high field effect mobility (μ_{FE}) compared with the SnO films grown at lower temperatures because of their large grain size and lower impurity contents. However, the SnO films grown at 210 °C still contain defects and hole carriers, especially near the back-channel surface. The post-deposition process – back-channel surface passivation with ALD-grown Al_2O_3 followed by post-deposition annealing at 250 °C – considerably alleviates the defects and hole carriers, resulting in superior TFT performance (I_{on}/I_{off}: 2×10^6, subthreshold swing: 1.8 $Vdec^{-1}$, μ_{FE}: ~ 1 $cm^2V^{-1}s^{-1}$). We expect that the SnO ALD and subsequent process will provide a new opportunity for producing high-performance p-type oxide TFTs.

9:20am **TF+EM+MI-WeM5 Recent Progresses of Atomic Layer Deposited Oxide Semiconductors for Emerging Display Applications**, ***Jin-Seong Park***, *J. Sheng, J.H. Lee,* Hanyang University, Republic of Korea **INVITED**

Recently, transparent amorphous oxide semiconductors have been widely studied for potential use in flat-panel displays, such as active-matrix organic light emitting diodes or liquid crystal displays. Semiconductors based on indium and zinc oxide compounds have been intensively studied since the report on transparent flexible amorphous InGaZnO TFTs based on physical vapor deposition (Hosono group) in 2004.

Among various thin film deposition methods, Atomic Layer Deposition (ALD) has remarkably developed in semiconductor and nano-structure applications since early 1990. The unique properties, including controlling atomic-level-thickness, manipulating atomic-level-composition control, and depositing impurity-free films uniformly, may accelerate ALD related industries and applications in functional thin film markets. One of big and challenging markets, display industry, has been just started to look at the potential to adopt ALD based films in emerging display applications, such as transparent and flexible displays.

In this talk, I will introduce various oxide semiconductor materials such ZnO, SnOx, InOx, ZnSnO, InZnOx, deposited by ALD processes. InOx and SnOx semiconductors were prepared by using a liquid indium precursor ([1,1,1-trimethyl-N-(trimethylsilyl) silanaminato]-indium) and tin precursor (N, N'-tert-butyl-1,1-dimethylethylenediamine stannylene-tin), respectively. The former exhibited highly transparent conducting oxide film property and the latter did the p-type polarity under a water reactant. The Indium oxide films were grown by ALD using as the metal precursor and hydrogen peroxide (H_2O_2) as the oxidant. It is found that the electrical properties of the indium oxide layers strongly depend on the ALD growth temperature. At relatively low growth temperatures below 150 ^oC, indium oxide behaves as a transparent semiconducting oxide. Secondly, amorphous indium zinc oxide thin films were deposited at different temperatures. The ALD process of IZO deposition was carried by repeated supercycles, including one cycle of indium oxide and one cycle of zinc oxide. The IZO growth rate deviates from the sum of the respective In_2O_3 and ZnO growth rates at ALD growth temperatures of 150, 175, and 200 °C. Thin film transistors were fabricated with the ALD-grown IZO thin films as the active layer. The amorphous IZO TFTs exhibited high mobility of 42.1 cm^2 V^{-1} s^{-1} and good positive bias temperature stress stability. Finally, flexible InOx and IZO TFTs on polymer substrates were investigated under various mechanical stress conditions, showing interesting degradations of TFTs. It will be discussed about the following issues.

11:00am **TF+EM+MI-WeM10 Silicon Nitride Thin Films Grown by Hollow Cathode Plasma-Enhanced ALD using a Novel Chlorosilane Precursor**, ***Xin Meng***, *H.S. Kim, A.T. Lucero, J.S. Lee, Y.-C. Byun, J. Kim,* University of Texas at Dallas, *B.K. Hwang, X. Zhou, M. Telgenhoff, J. Young*, Dow Chemical

Plasma-enhanced ALD (PEALD) has become an attractive method of depositing silicon nitride (SiN_x) due to its ability to grow high-quality films at low temperatures (≤400°C) for various applications [1]. The use of a chlorosilane precursor, is considered a suitable approach for high-volume manufacturing in the semiconductor industry. Chlorosilane precursors can be applicable to either PEALD SiN_x or thermal ALD SiN_x process. In this work, we have investigated the growth of SiN_x thin films using a novel chlorosilane precursor pentachlorodisilane (PCDS, HSi_2Cl_5)(synthesized by Dow Corning Corporation, vapor pressure ~10 mmHg at 20 °C) in comparison with hexachlorodisilane (HCDS, Si_2Cl_6). A home-made PEALD system equipped with a hollow cathode plasma source (Meaglow Ltd.) was used in this study.

We analyzed the growth per cycle (GPC) and refractive index (R.I.) as a function of the silicon precursor or plasma exposure time, deposition temperature and plasma power. We also investigated the wet etch rate (WER) in dilute hydrochloric acid as a function of the hydrogen content determined by Fourier Transform Infrared Spectrometry (FTIR), and film density determined by X-ray reflectivity (XRR). Using an N_2/NH_3 plasma, saturated growth behavior was demonstrated by PCDS and HCDS with a precursor exposure of ~3×10^5 L. GPC was nearly independent of both deposition temperature and RF power, within the investigated regime. Compared to HCDS, PCDS demonstrated approximately 20–30% higher GPC under the same process condition while maintaining comparable WER.

In addition, it was found that the films with higher hydrogen content had a general tendency to have a higher WER while the films with a higher density or higher R.I. tended to have a lower WER. The oxygen content of the bulk SiN_x films determined by ex-situ X-ray photoelectron spectroscopy (XPS) was approximately 3~5 at. % and didn't have a direct correlation with the WER. Furthermore, MIM capacitors (Al/SiN_x/degenerated Si) using PEALD SiN_x films grown with PCDS were fabricated. The capacitors exhibited excellent electrical properties, such as a low leakage current density of 10^{-9}–10^{-10} A/cm^2 at 3 MV/cm, and a high breakdown electric field ~13 MV/cm.

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11:20am **TF+EM+MI-WeM11 Removal of Charge Centers in Hafnia Films by Remote Plasma Nitruration**, ***Orlando Cortazar-Martínez***, *J.A. Torres-Ochoa, C.L. Gomez-Muñoz, A. De Luna-Bugallo, A. Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

We investigated the effect of soft nitridation on the electrical properties of hafnia-based MOS capacitors. Starting from a cleaned Si (100) wafer a 2 nm of HfO_2 thin film is grown by ALD using tetrakis (dimethylamido) hafnium(IV) and water type I as precursors. The growth was performed at a temperature of 250 °C with a 20 sccm flow of ultra-high purity nitrogen (UHP-N). Hafnium oxide soft nitridation was performed by a remote plasma (Litmas) using a power of 2500 W, a substrate temperature of 500 °C, the ultra-high purity nitrogen flow was set at 140 sccm and the working pressure is fixed at $3.5x10^{-2}$ Torr. A 300 nm titanium nitride (TiN) layer is deposited in-situ after nitration in a sputtering system, avoiding undesired contamination. Finally, MOS capacitors were defined using photolitography and etching process.

Capacitance vs voltage measurements characterization was carrying out at different frequencies (1 kHz to 1 MHz). MOS capacitors before nitriding shows a decreasing value in their accumulation capacitance when the frequency is increased. This behavior is attributed to the defects states located inside the oxide layer[1]. In contrast, MOS capacitors measured after nitriding barely shows dispersion in their accumulation regime as the frequency was varied. Also, it can be noted that the threshold voltage remains unchanged.

Films thickness and composition were characterized by ARXPS[2]. The initial thickness and composition were 20.7 Å and $HfO_{2.09}$. After nitridation the thickness changed to 19.8 Å with a composition of $HfO_{1.4}N_{0.48}$. XPS spectra show that the N 1s peak observed at 396.8 eV is associated with the N-Hf bond[3], showing a robust evidence of a substitutional incorporation of nitrogen species into the HfO_2 with a saturation process like the one reported in silicon oxide nitridation[4]. Results can be correlated with the soft nitridation process used during fabrication with the remote plasma in which the substitutional nitrogen to oxygen interchange in the HfO_xN_y films keeping the tetrahedral structure from the ALD hafnium as the same as the original but decreasing the amount of the defect states inside the oxide layer.

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11:40am **TF+EM+MI-WeM12 Seam-free Bottom-up Filling of Trenches with HfO_2 using Low Temperature CVD**, ***Tushar Talukdar***, *W.B. Wang, E. Mohimi, G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign

Filling a deep structure is always a transport-reaction problem, one that is sensitive to the geometry of the structure. For example, with parallel sidewalls, a conformal process can mostly fill the structure, but as film growth diminishes the width of the remaining opening, the AR rises towards infinity; under that condition, no process can eliminate the "seam" in the center. We have shown, using both diffusion and molecular transport models, that a V-shape with an outwards taper (e.g., 3° or more) is needed for conformal coating to work [1]. The other alternative is to develop a process in which film growth is faster at the bottom of the structure: a *superconformal* process in which the growth rate increases progressively with depth. We previously demonstrated a superconformal process for MgO based on (i) a competition for surface adsorption sites between precursor and water co-reactant, and (ii) a large ratio in diffusivity between the high-mass precursor and low-mass water [2].

Here, we attempt to develop superconformal growth of HfO_2 from tetrakis dimethylamido hafnium (TDMA-Hf) based on our previous method for MgO. We choose the TDMA-Hf precursor because it affords excellent film quality in ALD, e.g., HfO_2 for gate dielectrics. However, the reaction kinetics of this precursor with water as the co-reactant differ strongly from the competitive adsorption model that is the basis for superconformal MgO deposition. Instead, the film growth rate is nearly independent of precursor flux and increases almost linearly with water flux.

For HfO_2, we therefore introduce a new approach in which water is injected in a forward-directed flux through a tube aligned with the trench axis. Water is transported ballistically to the trench bottom, where it partially reflects and creates a *virtual source at the trench bottom*. At the same time, the coating conditions are nearly conformal. The combination of a virtual source at the bottom and nearly conformal growth affords a V-shaped profile and excellent filling characteristics. We also introduce a simple kinetic model that predicts the fill profile based on the measured growth rate kinetics.

A limitation to this method is that rapid film growth also occurs on the exposed top surfaces. For a structure with parallel sidewalls, this tends to narrow the opening such that pinch-off can occur prior to complete fill. One solution is to use a structure with an outwards taper to the sidewalls. Another potential solution is to suppress growth at the trench opening using an inhibitor, which we will demonstrate.

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12:00pm **TF+EM+MI-WeM13 Low-κ Organosilicon Thin Films Deposited by iCVD for Electrical Insulation of Through Silicon Vias**, ***Mélanie Lagrange***, *C. Ratin, M. Van-Straaten, C. Ribière, T. Mourier, V. Jousseaume*, CEA-Leti, France

3D integration is considered as an attractive technological route to fabricate cost-effective, high-performance products with reduced size.[1] This technology is based on the use of Through Silicon Vias (TSV), which are vertical connections between electronic components. One of the key steps in TSV fabrication is their electrical insulation from the Si substrate. Depending on the TSV integration scheme used, the allowed thermal budget is limited. For instance, via-middle and via-last integrations need process temperatures lower than 400°C and 200°C, respectively. Moreover, considering the high Aspect Ratio ($AR \geq 10$) required by the TSV-middle integration, a highly conformal deposition technique is needed.

Initiated Chemical Vapor Deposition, iCVD, is a low-energy and solvent-free polymer film fabrication process. It is able to deposit solid materials with high step coverage of deep blind features on low-temperature substrates. In the last decade, this versatile method has enabled the deposition of numerous types of polymers, including organosilicons (OSi)[2]. OSi polymers are low-κ materials having shown to be useful in a broad range of applications, including insulation layers in electronic devices.[3]

In this study, dielectric thin films were deposited from vinyl-based OSi precursors using iCVD. The impact of different process conditions on deposition rate, chemical composition and electrical properties of the films have been investigated. Thin films deposited at low temperature, typically < 60°C, can present low dielectric constants (< 3) without the need of any post-deposition treatment. However the films have to face 400°C thermal budget from BEOL process in via-middle integration, therefore a need for sample stabilization emerged. The impact of thermal or UV-assisted annealing on the films properties was investigated in order to understand the thermal stability of the materials and extrapolate their behavior during TSV fabrication and its integration in a full device fabrication flow (BEOL and Back side process). A study of the step coverage achieved by iCVD-deposited thin films in 10*100 µm TSV was performed. It shows that iCVD is promising to deposit materials with high conformity in high AR TSV. Finally, the integration of these OSi polymers in functional TSV, using a standard metallization process on 300 mm wafers, is presented.

The OSi films depositions were processed in a vertical flow reactor, under a collaboration with Kazuya Ichiki, Bruce Altemus and Jacques Faguet, at TEL Technology Center, America.

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Electronic Materials and Photonics Division
Room: 14 - Session EM+2D+MI+MN-WeA

Materials and Devices for Quantum Information Processing
Moderators: Rachael Myers-Ward, U.S. Naval Research Laboratory, Steven Vitale, MIT Lincoln Laboratory

2:20pm **EM+2D+MI+MN-WeA1 Controlling the Valley Degree of Freedom in 2D Transition Metal Dichalcogenides**, ***Tony Heinz***, Stanford University / SLAC National Accelerator Laboratory **INVITED**

Monolayer transition metal dichalcogenide crystals in the MX_2 family with M = Mo, W and X = S, Se have been shown to provide attractive possibilities for access to the valley degree of freedom both optically and through the valley Hall effect. In this paper we will summarize recent advances in the electrical and optical control of the valley degree of freedom in this class of materials.

The optical selection rules in the transition metal dichalocogenide monolayers permit selective creation of excitons in either the K or K' valley through the use of circularly polarized light. Excitons consisting of coherent superpositions of both valleys can also be produced through excitation with linearly polarized light. While these results have already been demonstrated experimentally, to date there has been no report of an approach to *manipulate* the valley exciton pseudospin after its creation. In this paper we present our recent use of the optical Stark effect to dynamically modify the valley pseudospin. The approach is based on selectively altering the energy of one valley vis-a-vis the other through application of a sub-gap optical pulse with circular polarization. This perturbation leads to a rapid rotation of the exciton valley pseudospin, as revealed by a change in the polarization state of the exciton emission.

In a second line of investigation, we have applied to spin-valley Hall effect in transition metal dichalocogenide monolayers to produce spatially separated regions with enhanced valley (and spin) populations. This is achieved by running a current through a hole-doped monolayer and relying on the anomalous velocity terms to separate the holes spatially. The resulting spin-valley spatial profile has been directly imaged on the micron scale and characterized using measurements based on the optical Kerr effect. The magnitude of this spin-valley imbalance and its dependence on doping and bias fields have been investigated and compared with theoretical predictions.

3:00pm **EM+2D+MI+MN-WeA3 VOI-based Valleytronics in Graphene**, ***Yu-Shu Wu***, National Tsing-Hua University, Taiwan, Republic of China **INVITED**

Electrons in gapped graphene carry a unique binary degree of freedom called valley pseudospin, in association with the two-fold valley degeneracy at the Dirac points (K and K') of Brillouin zone. Such pseudospin carries an intrinsic angular momentum and responds to external electromagnetic fields in ways similar to those of an ordinary electron spin [1,2]. We examine the response and address the important issue of valleytronics - the electrical manipulation of valley pseudospin. A unified methodology called VOI based valleytronics will be presented, which exploits the valley-orbit interaction (VOI) between an in-plane electric field and a valley pseudospin for the implementation of valleytronics. Based on the VOI mechanism, a family of fundamental structures have been proposed with important device functions, such as valley qubits, valley filters, and valley FETs [3]. We will report recent theoretical developments in these structures.

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4:20pm **EM+2D+MI+MN-WeA7 Creating Quantum Technologies with Spins in Semiconductors**, *B.B. Zhou*, ***David Awschalom***, University of Chicago **INVITED**

There is a growing interest in exploiting the quantum properties of electronic and nuclear spins for the manipulation and storage of information in the solid state. Such schemes offer fundamentally new scientific and technological opportunities by leveraging elements of traditional electronics to precisely control coherent interactions between electrons, nuclei, and electromagnetic fields. Although conventional electronics avoid disorder, recent efforts embrace materials with incorporated defects whose special electronic and nuclear spin states allow the processing of information in a fundamentally different manner because of their explicitly quantum nature [1]. These defects possess desirable qualities – their spin states can be controlled at and above room temperature, they can reside in a material host amenable to microfabrication, and they can have an optical interface near the telecom bands. Here we focus on recent developments that exploit precise quantum control techniques to explore coherent spin dynamics and interactions. In particular, we manipulate a single spin in diamond using all-optical adiabatic passage techniques [2], and investigate the robustness of the acquired geometric (Berry) phase to noise as well as novel strategies to overcome traditional speed limits to quantum gating. Separately, we find that defect-based electronic states in silicon carbide can be isolated at the single spin level [3] with surprisingly long spin coherence times and high fidelity, can achieve near-unity nuclear polarization [4] and be robustly entangled at room temperature [5]. Finally, we identify and characterize a new class of optically controllable defect spin based on chromium impurities in the wide-bandgap semiconductors silicon carbide and gallium nitride [6].

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5:00pm **EM+2D+MI+MN-WeA9 Diamond as an Electronic Material: Opportunities and Challenges**, ***Steven Vitale***, *J.O. Varghese, M.F. Marchant, T. Wade, M.W. Geis, T.H. Fedynyshyn, D.M. Lennon, M.A. Hollis*, MIT Lincoln Laboratory

Diamond possesses extraordinary semiconductor properties including carrier mobility, saturation velocity, and thermal conductivity which far exceed those of silicon and essentially all other semiconductor materials. In spite of these incredible qualities diamond has not yet become a mainstream transistor material, for two primary reasons. First, existing small single-crystal substrates have not been able to take advantage of commercial microelectronics processing equipment and growth of wafer-scale single-crystal diamond has not been vigorously pursued. Second, deep donor and acceptor levels in diamond imply that the impurity ionization fraction is quite low at room temperature which results in low carrier density in conventional FET architectures.

However the situation has changed dramatically in the past few years. Plasma-enhanced CVD promises to create large-wafer single-crystal diamond through mosaic or novel catalytic growth.[1] Additionally, the discovery of the diamond surface FET has addressed the problem of low carrier density.[2] Together, these advancements may allow development of practical diamond transistors with unparalleled performance for high-power, high-frequency applications. Many unit process and process integration challenges remain to develop diamond surface FETs into commercial technology. This paper will report on the state of the art in diamond surface FET technology and will examine current unmet needs.

We have developed diamond surface FETs with current densities in excess of 100 mA/mm. This is enabled by a novel surface activation process using a high concentration of NO_2 in air to react with a hydrogen-plasma-treated diamond surface. The electron accepting nature of the modified surface abstracts an electron from the diamond, resulting in a 2D hole gas (2DHG) in the diamond. We measure a hole mobility of 30-130 cm^2/V-s and a repeatable surface resistance of ~ 1.5 $k\Omega\ sq^{-1}$ using this technique. 2DHG formation has been demonstrated using other surface moieties as well, including photoacid radical generators and trinitrotoluene. Pros and cons of these different surface adsorbates will be discussed. The performance of Au, Mo, Pt, Al, Pd, Ti, Cr contacts, as well as combinations of these metals will be presented, with a record-low diamond contact resistance of 0.6 ohm-mm and good ohmic behavior.

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5:20pm **EM+2D+MI+MN-WeA10 Studies on Influence of Processing on Optical Characteristics of Electron Irradiated 4H-SiC Nanostructures**, ***Shojan Pavunny***, ASEE Research Fellow at U.S. Naval Research Laboratory, *H. Banks*, NRC Research Fellow at U.S. Naval Research Laboratory, *P.B. Klein*, U.S. Naval Research Laboratory, *K.M. Daniels*, NRC Research Fellow at U.S. Naval Research Laboratory, *M.T. DeJarld*, ASEE Research Fellow at U.S. Naval Research Laboratory, *E.R. Glaser*, *S.G. Carter*, *R.L. Myers-Ward*, *D.K. Gaskill*, U.S. Naval Research Laboratory

Spin-coherent single silicon defect centers (V_{Si}) in wide bandgap silicon carbide polytypes have recently drawn great research interest for future applications in information technologies such as scalable quantum computing, sensing and metrology. Identification of these deep defects, gaining a thorough knowledge of their characteristics, active control of their concentrations, isolation of single spin defects and understanding the effects of semiconductor processing on their properties are crucial challenges for the realization of SiC based quantum electronic and integrated photonic devices. These color centers coupled to photonic crystal cavities (PCC) have the capability of high efficiency emission of zero phonon lines which can significantly improve the performance of on-chip photonic networks and long-distance quantum communication systems, as compared to conventional solid-state emitters. Here we investigate the impact of fabrication process on the photoluminescence properties of PCCs realized using three techniques: hydrogen implantation to form thin SiC layers on an oxide layer that can be easily etched away to form an air gap under the PCC, wafer bonding and mechanical thinning of the SiC, also on an oxide layer, and selective electrochemical anodization of an n-p epitaxial SiC structure to form an air gap. We also comment upon the impact of electron irradiation for these three fabrication techniques.

5:40pm **EM+2D+MI+MN-WeA11 Ab Initio Simulations of Point Defects in Solids Acting as Quantum Bits**, ***Adam Gali***, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Hungary **INVITED**

Luminescent and paramagnetic point defects in insulators and semiconductors may realize quantum bits that could be the source of next generation computers and nanoscale sensors. Detailed understanding of the optical and magnetic properties of these defects is needed in order to optimize them for these purposes.

In this talk I show our recent methodology developments in the field to calculate the ground and excited state of point defects and to determine their Auger-rates, hyperfine tensors and electron spin – electron spin couplings, and intersystem crossing rates. We show recent results on the nitrogen-vacancy center in diamond as well as divacancy and other defects in silicon carbide that we have found a very promising alternative to the well-established nitrogen-vacancy center for integration of traditional semiconductor and quantum technologies into a single platform.

2D Materials Focus Topic
Room: 15 - Session 2D+MI-ThM

Novel Quantum Phenomena in 2D Materials
Moderator: Kai Xiao, Oak Ridge National Laboratory

8:00am **2D+MI-ThM1 Quantum Plasmonics with 2D Materials**, ***Dmitri Voronine***, University of South Florida

Quantum plasmonics effects were previously investigated in coupled metallic nanostructures with sub-nanometer gaps leading to large electron tunneling contributions. Two-dimensional transition metal dichalcogenides are promising materials with interesting optoelectronic, catalytic and sensing applications which may be integrated with plasmonic nanostructures and used in the quantum plasmonics regime. Their nanoscale optical characterization using tip-enhanced photoluminescence (TEPL) and tip-enhanced Raman scattering (TERS) spectroscopies provides detailed local structure-function information which is not available using far-field diffraction-limited techniques. Nanoscale optical imaging provides an improved understanding of the optoelectronic properties of edge states, defects and grain boundaries. Here we report nanoscale TEPL and TERS characterization of monolayer and few-layer 2D materials such as MoS2, WS2, MoSe2 and WSe2 and their alloys and heterostructures with subdiffraction spatial resolution due to the strong signal enhancement via surface plasmon confinement of the nano-size metallic tip. We investigate the limits of signal enhancement on various substrates by varying the tip-sample gap and reveal quantum plasmonic behavior for sub-nanometer gaps. We show that quantum plasmonics provides a new mechanism of the generation and control of excitons and trions in 2D materials via electron tunneling. We investigate various quantum plasmonics regimes with picometer-scale indentation control. These results may be used for improving the nano-optical properties of 2D materials and for designing novel quantum optoelectronic devices.

8:20am **2D+MI-ThM2 Investigation and Manipulation of One-Dimensional Charge Density Waves in MoS$_2$**, ***Wouter Jolie***, *C. Murray, J. Hall,* Institute of Physics II, University of Cologne, Germany*, F. Portner,* Institute for Theoretical Physics, University of Cologne, Germany*, B. Pielić,* Center of Excellence for Advanced Materials and Sensing Devices, Institute of Physics, Zagreb, Croatia*, N. Atodiresei,* Peter Grünberg Institute and Institute for Advanced Simulation, Forschungszentrum Jülich, Germany*, M. Kralj,* Center of Excellence for Advanced Materials and Sensing Devices, Institute of Physics, Zagreb, Croatia*, A. Rosch,* Institute for Theoretical Physics, University of Cologne, Germany*, C. Busse,* Institut für Materialphysik, Westfälische Wilhelms-Universität Münster, Germany*, T. Michely,* Institute of Physics II, University of Cologne, Germany

Grain boundaries in monolayer transition metal dichalcogenides (TMDC) are predicted to host one-dimensional metallic states embedded in an otherwise insulating layer. As was shown recently for MoSe$_2$ [1,2], these states may be electronically unstable, undergoing a Peierls transition which leads to a charge density wave (CDW) at low temperatures.

We investigate epitaxial monolayer-MoS$_2$ on graphene on Ir(111) with scanning tunneling microscopy and spectroscopy (STM/STS). We find a large bandgap in MoS$_2$ showing that it is well decoupled from the substrate. The MoS$_2$ islands feature long, straight, highly symmetric twin boundaries. Along these we measure a small bandgap together with periodic beatings in the local density of states, both characteristic of CDWs. We investigate different types of line defects in MoS$_2$ and find correspondingly different CDWs. These quasi-freestanding wires offer an opportunity to study the simple yet rich physics of CDWs, not often seen in true 1D form experimentally. Specifically, we investigate their properties based on symmetry analysis, the impact of point defects, temperature-dependence, phase-behavior and their response to doping.

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8:40am **2D+MI-ThM3 Configuring Electronic States in an Atomically Precise Array of Quantum Boxes**, ***Seyedeh Fatemeh Mousavi***, *S. Nowakowska, A. Wäckerlin,* University of Basel, Switzerland*, I. Piquero-Zulaica,* Materials Physics Center, San Sebastián, Spain*, J. Nowakowski,* Paul Scherrer Institut (PSI), Switzerland*, S. Kawai,* University of Basel, Switzerland*, C. Wäckerlin,* Paul Scherrer Institut (PSI), Switzerland*, M. Matena, T. Nijs, S. Fatayer, O. Popova, A. Ahsan, T. Ivas, E. Meyer,* University of Basel, Switzerland*, M. Stöhr,* University of Groningen, Netherlands*, J.E. Ortega,* Materials Physics Center, San Sebastián, Spain*, J. Björk,* Linköping University, Sweden*, L.H. Gade,* Universität Heidelberg, Germany*, J. Lobo-Checa,* Universidad de Zaragoza, Spain*, T.A. Jung,* Paul Scherrer Institut (PSI), Switzerland

Quantum boxes (QBs) [1] have been arranged in extended 2D arrays by the self-assembled formation of a porous on-surface coordinated network [2]. Xe atoms were used as an adsorbate for their well-defined interaction with the surface state electrons of Cu(111), which is dominated by Pauli repulsion. The electronic states contained in these arrays can be configured by the localized perturbation by the targeted filling level of the individual QBs with Xe atoms after Xe repositioning, each quantum box exhibits maximal 12 filling levels, which incrementally perturb the quantum box state(s) via Pauli repulsion. It is shown that specific filling patterns of the network of the QBs which are coupled in an inherently precise way by self assembly [3] specifically perturb, and thus modify the localized and delocalized quantum box states (QBSs). In particular the energy levels of the QBSs is modulated also it is demonstrated that the inter-box coupling can be sustained or significantly weakened by an appropriate arrangement of empty and filled boxes. We gain unprecedented insight into the physics of interacting quantum states on the local level as well as in their cooperative interaction by using complementary scanning tunneling microscopy/spectroscopy (STM/STS) and angle-resolved photoemission spectroscopy (ARPES) measurements. Our approach establishes that such self-assembled two-dimensional quantum box architectures may serve as nanoscale analog of breadboards that are commonly employed in electronic circuitry and guide towards the fabrication of quantum devices.

References

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9:00am **2D+MI-ThM4 A Quantum Berry Phase Switch in Circular Graphene Resonators**, ***Daniel Walkup****, *F. Ghahari, C. Gutierrez,* NIST/CNST*, J.F. Rodriquez-Nieva,* Harvard University*, Y. Zhao, J. Wyrick, F.D. Natterer, W.G. Cullen,* NIST/CNST*, K. Watanabe, T. Tanaguchi,* National Institute for Materials Science, Japan*, L.S. Levitov,* MIT*, N.B. Zhitenev, J.A. Stroscio,* NIST/CNST

In graphene and other 2D Dirac materials, the band structure has the property that momentum-space paths enclosing the Dirac point pick up a Berry phase of π. In a uniform magnetic field, this leads to a special quantization rule and an N=0 Landau level at the Dirac point. In a circular graphene resonator, weak magnetic fields can tune the quantized electron orbits between states with Berry phases of zero and π, leading to a discontinuous jump in the quantum energy level as a function of applied field. Here we report scanning tunneling microscopy and spectroscopy (STM/S) studies of circular resonators fabricated in p-n junction rings in graphene/hBN backgated devices. We observe direct signatures of a Berry-phase-induced switching of the resonator states measured with scanning tunneling spectroscopy as a function of magnetic field. The telltale signature is a sudden and large increase in the energy of angular-momentum states in the graphene p-n junction resonators when a small critical magnetic field is reached, in agreement with theoretical calculations of Dirac potential wells.

9:20am **2D+MI-ThM5 Nanostructured Graphene: A Platform for Fundamental Physics and Applications**, ***Antti-Pekka Jauho***, Technical University of Denmark, Denmark **INVITED**

Despite of its many wonderful properties, pristine graphene has one major drawback: being a semimetal it does not have a band gap, which complicates its applications in electronic devices. Many routes have been suggested to overcome this difficulty, such as cutting graphene into nanoribbons, using chemical methods or periodic gates, and - which is the paradigmatic example of this talk - by making regular nanoperforations, also known antidot lattices [1]. All these ideas work beautifully in theory, but realizing them in the lab

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* **NSTD Postdoc Finalist**

is very difficult because fabrication steps inevitably induce disorder and other nonidealities, with potentially disasterous consequences for the intended device operation. In this talk I introduce these ideas and review the state-of-the –art both from the theoretical and the experimental points of view. I also introduce some new ideas, such as triangular antidots [2], and nanobubbles formed in graphene [3]. Our simulations, relying on advanced numerical techniques, show that it may be possible to generate very high quality spin- and valley polarized currents with these structures – something that has not yet been achieved in the lab. Importantly, our simulations involve millions of atoms which is necessary in order to address structures feasible in the lab.

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11:00am **2D+MI-ThM10 Anomalous Kondo Resonance Mediated by Graphene Nanoribbons**, ***Yang Li***, Ohio University and Argonne National Laboratory, *A. Ngo*, Argonne National Laboratory, *K.Z. Latt*, Ohio University, *B. Fisher*, Argonne National Laboratory, *S.W. Hla*, Argonne National Laboratory and Ohio University

Atomically precise graphene nanoribbons (AGNR) are formed by one dimensional graphene sheets of carbon atoms and they can exhibit semiconducting characteristics with varying bandgaps. For the device and sensor applications, it is important to explore AGNR heterostructures. Here, we form molecular heterostructures using magnetic molecules and on-surface synthesized AGNRs on a Au(111) surface. Then the electronic and spintronic properties of the AGNR-magnetic molecule-Au(111) heterostructures are investigated by using scanning tunneling microscopy, tunneling spectroscopy and atomic/molecular manipulation schemes at 5 K substrate temperature in an ultrahigh vacuum environment. Although the AGNRs on Au(111) surface have a semiconducting characteristic with a large bandgap, we discover the unexpected Kondo resonance on molecules adsorbed on AGNRs. Interestingly, the observed Kondo temperatures of the molecules appear the same as the ones adsorbed on AGNRs and Au(111) surface including the atomic scale differences due to adsorption site. The experimental results are explained by density functional theory and numerical renormalization group theory calculations. We acknowledge the support of DOE SISGR grant: DE-FG02-09ER16109.

11:20am **2D+MI-ThM11 Valley Photoluminescence Polarization in Monolayer WSe$_2$**, ***Aubrey Hanbicki***, *M. Currie*, Naval Research Laboratory, *G. Kioseoglou*, University of Crete, *A.L. Friedman, B.T. Jonker*, Naval Research Laboratory

Monolayer materials such as WS$_2$ or WSe$_2$ are direct gap semiconductors with degenerate, yet inequivalent *k*-points at *K* and *K'*. The valence band maxima for *K* and *K'* have spin states of opposite sense enabling one to selectively populate each valley independently with circularly polarized light. Subsequent valley populations can be determined via the polarization of emitted light. Optical emission is dominated by neutral and charged exciton (trion) features, and changes in emitted polarization provide insight into the fundamental processes of intervalley scattering. We measure the circularly polarized photoluminescence of WSe$_2$ monolayers as a function of excitation energy for both continuous-wave (cw) and pulsed laser excitation sources. Using cw excitation, the temperature dependence of the depolarization of the trion follows the same trend as that of the neutral exciton and involves collisional broadening. However, the initial polarization of the trion is nearly twice the polarization of the neutral exciton at low temperature. When a pulsed laser is used as the excitation source, the initial polarization of the neutral exciton increases and becomes very similar to the trion. We propose either an up-conversion process or screening from the instantaneously large carrier density generated by the pulsed excitation to explain these data. The difference in polarization behavior is linked to the different way energy is deposited in the system during these measurements. We also discuss changes in the photoluminescence induced by pulsed laser excitation.

This work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #AOARD 14IOA018-134141.

11:40am **2D+MI-ThM12 Imaging Superconducting Topological Surface States in Non-centrosymmetric PbTaSe$_2$**, ***Tien-Ming Chuang***, Academia Sinica, Taiwan, Republic of China **INVITED**

The search for topological superconductors (TSCs) is one of the most exciting subjects in condensed matter physics. TSCs are characterized by a full superconducting gap in the bulk and topologically protected gapless surface (or edge) states. Within each vortex core of TSCs, there exist the zero energy Majorana bound states, which are predicted to exhibit non-Abelian statistics and to form the basis of the fault-tolerant quantum computation. So far, no stoichiometric bulk material exhibits the required topological surface states (TSSs) at E_F combined with fully gapped bulk superconductivity. Here, we use spectroscopic-imaging scanning tunneling microscopy to study the atomic and electronic structures of the non-centrosymmetric superconductor, PbTaSe2. Our results demonstrate PbTaSe2 as a promising candidate as a 2D TSC.

Electronic Materials and Photonics Division
Room: 14 - Session EM+MI+NS+SP+SS-ThM

Photonics, Optoelectronics, and Light Manipulation
Moderators: Yohannes Abate, Georgia State University, Nikolaus Dietz, Georgia State University

8:00am **EM+MI+NS+SP+SS-ThM1 Evolutionary Design of Multi-functional Optical Metasurfaces**, ***Teri Odom***, Northwestern University **INVITED**

Metasurfaces are an emerging class of flat optics that can manipulate light via subwavelength phase elements. Their 2D structures are usually determined by (1) calculating the phase change required at each location to obtain far-field properties from analytical equations and (2) structuring each building block to produce that wavefront change. However, computational or digital approaches to design metasurfaces based on search heuristics offer advantages in targeting and realizing properties not possible by analytical expressions. This talk will describe an evolutionary approach to design flat lenses based on subwavelength plasmonic building blocks. Our lattice evolution algorithm can achieve desired optical responses by tuning the arrangement of the phase units on a discrete square lattice. We will discuss two different systems with different classes of building units—holes and particles—to realize achromatic lattice lenses at up to three wavelengths and flat lenses in semiconductor plasmonic materials such as titanium nitride. We will describe prospects for scaling the production of these lenses as well as their ability to achieve dynamic optical responses.

8:40am **EM+MI+NS+SP+SS-ThM3 Dielectric Freeform Metasurfaces for Optical Sensing**, ***Arka Majumdar***, University of Washington, Seattle **INVITED**

The macroscopic volume of optical sensors, such as cameras, often originates from the requirement of having multiple optical elements and thick spherical geometries. In recent years, researchers have made subwavelength optical elements, commonly known as metasurfaces, with an ultra-thin form factor using well-developed semiconductor nano-fabrication technology. In parallel with the progress in such nano-photonic devices, researchers have also made vast improvements in the field of freeform optics. Freeform optics aim to expand the toolkit of optical elements beyond those exhibiting rotational symmetry. Most conventional optical elements have rotational symmetry for manufacturing reasons, but freeform optics emphasizes complex surface geometries, which are difficult to manufacture by traditional means. While both metasurface and freeform optics have progressed substantially in recent years, they have developed independently of one another as their respective research communities are disconnected.

In our work, we demonstrated how metasurface technology can be used for the realization of subwavelength scale freefrom optics, with applications in implantable bio-sensing and potentially in augmented reality systems. I will present some of our recent results on metasurface freeform optics that enable a large depth of focus and a tunable focal length lens. I will also show how these metasurfaces can be used to perform truly colored imaging, by virtue of the extended depth of focus. Finally, I will talk about our ongoing work on metasurface based cavity engineering.

9:20am **EM+MI+NS+SP+SS-ThM5 Moth eye-based, graded index surface treatments to control reflection and light extraction**, *L. Chan, C. Pynn, P. Shapturenka, R. Ley, S. Denbaars, D. Morse,* ***Michael Gordon***, University of California at Santa Barbara

This talk will highlight our recent work on bio-inspired surface treatments to control reflection and enhance light extraction at interfaces. An easy, scalable and defect-tolerant surface modification protocol, based on colloidal lithography and plasma etching, was developed to create synthetic 'moth-eye' (ME) anti-reflective structures in different material platforms for photonics and energy applications. Large increases in transmission, bandwidth, and omni-directional response were obtained in Si, Ge, GaAs, ZnS/ZnSe, and CdTe platforms for IR (2-50+ um), with performance better than commercial, interference-based coatings. Effective medium theory, finite difference time domain (FDTD) simulations, and quantitative measurements of transmission, reflection and diffuse scattering were used to understand the 'photon balance' of ME films to investigate how optical behavior depends on moth-eye geometry, (dis)order, and pattern fidelity. ME coatings were also implemented in blue-green InGaN/GaN quantum well LED structures on c-plane and semi-polar substrates to enhance light extraction and device efficiency. A 4.8-fold overall enhancement in light extraction (9-fold at normal incidence) compared to a flat surface was achieved using a feature pitch of 2530 nm—performance on par with current photoelectrochemical (PEC) roughening methods. The colloidal lithography roughening technique presented herein is independent of GaN crystal orientation and is therefore applicable to roughening semipolar and nonpolar GaN devices, on which PEC roughening is ineffective.

9:40am **EM+MI+NS+SP+SS-ThM6 Infrared Surface Plasmon-influenced Interfacial Chemistry of Semiconductor Nanocrystals**, *W. Hu, **Michael Filler***, Georgia Institute of Technology

Localized surface plasmon resonances (LSPRs) present exciting opportunities to improve the spatial and temporal control of chemistry at semiconductor surfaces. While the ultraviolet and visible LSPRs supported by metallic nanoparticles are known to impact surface chemistry, heavily-doped semiconductor nanocrystals promise similar capabilities in the near and mid-infrared. Here, we use time-resolved *in situ* infrared spectroscopy to study the influence of mid-infrared LSPRs on a model interfacial process: desorption. We find that the molecular desorption rate for a range of "beacon" molecules (e.g., indole, benzoic acid) on indium tin oxide (ITO) nanocrystals is enhanced by as much as 2x upon illumination with mid-infrared light (~0.6-0.1 eV) at room temperature. The desorption rate is linearly dependent on light intensity, indicating a single photon process. Experiments as a function of LSPR energy, nanocrystal film thickness, and adsorbate concentration provide clues as to the mechanism of the enhancement. Our findings open new avenues to leverage low energy photons for manipulating chemical reactions on the surfaces of heavily-doped semiconductors.

11:00am **EM+MI+NS+SP+SS-ThM10 Dynamically Tunable Polarization Response in a Si/Au Metamaterial**, ***Nicole Pfiester***, Tufts University, *C. Shemelya*, Technische Universität Kaiserslautern, Germany, *D. DeMeo, E. Carlson, T.E. Vandervelde*, Tufts University

Polarimetry is utilized across many fields, from chemical characterization to classification of astronomical objects to the detection of man-made items. Present technology requires a different filter for each polarization of light you wish to measure. This requires either a cluster of four pixels to differentiate between the polarizations incident on an area, reducing the final image resolution compared to a non-polarized image, or a filter wheel that adds weight and mechanical reliability issues. Metamaterials can be leveraged to design materials with a polarization sensitive response. Application of a bias voltage can further alter the material's interaction with incident light, resulting in a metamaterial whose response can be tuned dynamically. This technique can be used to create a filter that can be turned on and off for a given polarization. An integrated stack of these filters would allow the measurement of any polarization direction at the full resolution capacity of the detector with the advantages of on-chip integration.

We designed a metamaterial structure that generates a polarization-dependent response in the mid-infrared wavelength range. Off-setting the absorption and transmission peaks for the two polarizations allows equal transmission while the filter is in a static state, or without a bias voltage. The application of a bias changes the metamaterial response and blocks polarized waves parallel to one axis. A thin film semiconductor layer is required to achieve this effect. Previous work utilized thin film gallium arsenide, but poor film quality of the epitaxial layer, with surface roughness on the order of the metamaterial feature size, did not provide sufficient conductivity for an applied bias to impact the light interactions. We will present new results using thin film silicon with a gold nanostructure pattern. A static filter, one that does not require an applied voltage to operate as a polarizing filter, was fabricated to demonstrate the design suitability. We will report on our progress toward a dynamic filter and compare to previous results with III-V films.

11:20am **EM+MI+NS+SP+SS-ThM11 Imaging Stress Induced Lateral Quantum Barrier Manipulation of Indium Gallium Arsenide Quantum Wells, using Micro-Photoluminescence Spectroscopy**, ***Brian Rummel**, M. Rimada, S. Addamane, G. Balakrishnan*, University of New Mexico, *T. Sinno*, University of Pennsylvania, *S.M. Han*, University of New Mexico

We have previously demonstrated that a patterned elastic stress field can be used to change the near-surface atomic composition in epitaxial compound semiconductor films.[1] This compositional patterning laterally manipulates quantum barriers within the film in a press-and-print manner, completely eliminating the need for Stranski-Krastanov growth. For the proof-of-concept, the said mechanism was used to diffuse Ge in a SiGe substrate to form regions of Ge-depleted, pure Si surrounded by SiGe. This result opened the door to thermo-mechanically triggered, rewritable circuitry for a wide variety of applications. For the current effort on InGaAs quantum well systems, an array of Si pillars is pressed against a GaAs/$In_{.20}Ga_{.80}As$/GaAs substrate in a mechanical press, and the assembly is heated to elevated temperatures. The applied elastic stress field promotes the diffusion of larger In atoms away from the compressed regions, leaving In-depleted GaAs in localized regions of the quantum well. Careful assembly and design of the Si nanopillar array would controllably define GaAs and InGaAs regions, producing laterally organized quantum structures. Photoluminescence spectroscopy is used to confirm the diffusion of In and compositional variation, based on the wavelength shift of the emission line from the InGaAs quantum well. In this presentation, we will further discuss how micro-photoluminescence imaging can be used to directly image regions of In-enriched regions as well as In-depleted regions found under the elastically compressed areas. This method may allow us to register the compositionally altered regions for addressable circuitry.

[1] S. Ghosh, D. Kaiser, J. Bonilla, T. Sinno, and S. M. Han, "Stress-Directed Compositional Patterning of SiGe Substrates for Lateral Quantum Barrier Manipulation," *Appl. Phys. Lett.***107,** 072106-1:5 (2015).

11:40am **EM+MI+NS+SP+SS-ThM12 Silicon-Based Infrared Photodetectors Enabled by Hot Electrons**, ***Seok-Jun Han**, S.M. Han, S.E. Han*, University of New Mexico

Infrared (IR) detectors typically employ low band gap materials, such as InGaAs, InSb, or HgCdTe. However, these materials include elements that are rare, expensive, or toxic. Past research indicates that low-cost, abundant crystalline Si (c-Si) could be used for IR detection when metal electrodes are appropriately nanostructured. In this type of photodetection, the IR with energies below the Si band gap is strongly absorbed by the metal structures. The photoexcited electrons in the metal can then be injected into the conduction band of c-Si before being thermalized, and electric current can be generated. These non-thermalized hot electrons enable the detection of IR light with energies below the c-Si band gap. For efficient transport of electrons in the metal before thermalization, the metal layer should be as thin as approximately the electron mean free path. To induce strong optical absorption in such a thin metal layer, surface plasmon polaritons (SPPs) can be excited at the metal surface. Previous studies on hot electron photodetection utilized small-scale metamaterials or deep trench resonators to have strong resonant absorption of SPPs in thin metal films on c-Si at the desired frequencies. However, these structures had to be fabricated with high precision (e.g., e-beam lithography) because the metal structure size determines resonance. In this study, we pursue a low-cost, manufacturable path, which can tolerate practical fabrication errors. We make use of metal metasurfaces that can be fabricated by scalable, inexpensive techniques and achieve a broad-band IR absorption of over 95% in 15-nm-thick metal films. This unprecedented strong and broad-band absorption is enabled by a new scheme which uses multiple modes of SPPs while the light takes multiple passes within the c-Si substrate. During the passage, light is preferentially absorbed by the thin metal layer that is on one side of the substrate. Absorption on the other side is efficiently eliminated by using a dielectric layer. In our effort, the surface of the c-Si substrate where thin meal film is deposited is structured by a simple optical lithography. The structured surface admits the incident light into the substrate and prevents the light from leaking out of the substrate. In our scheme of multiple light passes, extremely strong resonances are not necessary and fabrication errors would not destroy the optical properties appreciably. In this talk, we will discuss the details of the optical absorption in our scheme. We will also present our experimental results on the electronic characteristics of our hot electron devices.

12:00pm **EM+MI+NS+SP+SS-ThM13 Low Temperature Wafer Bonding of LTG-GaAs to $Si_3N_4$for Terahertz Photoconductive Switch Application**, *X. Fu*, Illinois Institute of Technology and Argonne National Laboratory, *M. Haji-Sheikh, G. Westberg, S. Ross*, Northern Illinois University, *E. Landahl*, DePaul University, *K. Attenkofer*, Brookhaven National Laboratory, ***Thomas Wong***, Illinois Institute of Technology

Integrating GaAs optoelectronic devices with Si- based platforms has attracted much attention and efforts in recent years, as a thin layer of GaAs can exhibitsuperior bulk quality. Wafer bonding, an emerging approach of monolithic integration of GaAs on Si-based substrate, overcomes the lattice mismatch in heterogeneous growth. Several techniques with a post-bonding annealing at temperature exceeding 800°C have been demonstrated to achieve high-energy covalent bonds between III-V compound semiconductors and Si/SiO_2systems. However, the elevated temperature bonding process may create not only an inevitable thermal mismatch barrier but also damage the bonding materials. Thus, there is a need for improved technique to integrate GaAs with silicon based devices.

Low temperature grown (LTG) GaAs, which is typically obtained by molecular beam epitaxy (MBE) at temperatures as low as 200°C, offers very attractiveproperties such as ultra-short carrier lifetime, high electron mobility and high resistivity. It is verydesirable for applications such as ultrafast photoconductive switch, high efficiency solar cells and infrared LEDs. Pioneering work has demonstrated techniques to bond LTG-GaAs to Si/ SiO_2

at temperature as low as room temperature by means of plasma activation and by wafer bonding under vacuum. However, very few techniques have been developed to bond LTG-GaAs layer to Si_3N_4 substrate, mainly because Si_3N_4 is naturally hydrophobic and bonding has been considered unachievable10. The existing Si_3N_4 bonding techniques employ high temperature fusion of Si_3N_4 layers or apply a layer of bonding agent such as SiO_2.

In this paper, we report a room temperature approach to directly bond LTG-GaAs to Si_3N_4 by activating the surface of Si_3N_4 using weak HF acid solution. This method can be implemented on Si_3N_4 deposited over wide temperature range. Procedures to reduce the bonding voids and improve the bond strength are also described. In an application to utilize the developed method, we implemented this approach to fabricate a photoconductive switch on Si_3N_4 substrate bonded with LTG-GaAs and validated that the bonded LTG-GaAs retained the electro-optical properties. A THz opticalcross correlation test showed that the photoconductive switch responded swiftly to a femtosecond Ti-Sapphire laser pulse with a resolution of approximately 0.25ps. This wafer bonding method can be integrated with a wide range of microelectronic device fabrication thatrequires the bonding of LTG-GaAs layer with Si_3N_4.

Nanometer-scale Science and Technology Division
Room: 19 - Session NS+AS+EM+MI+SP+SS-ThM

Nanoscale Imaging and Characterization

Moderators: Stephane Evoy, University of Alberta, Canada, Indira Seshadri, IBM Research Division, Albany, NY

8:00am **NS+AS+EM+MI+SP+SS-ThM1 Characterizing Optoelectronically-Active Molecules via STM Imaging and Advanced Raman Spectroscopy Techniques**, *J. Schultz, P. Whiteman, Z. Porach, **Nan Jiang***, University of Illinois at Chicago

In response to the ever increasing demand for cleaner, cheaper energy generation, significant efforts have been made to fabricate and characterize materials that can be used for optoelectronic devices. Porphyrins, phthalocyanines, and their derivatives have been involved in many surface studies to investigate their optoelectronic properties for use in organic photovoltaics and other optoelectronic devices, such as organic light-emitting diodes (OLED). Our research take place in a commercial ultrahigh vacuum (UHV) scanning tunneling microscopy (STM) chamber. Molecules were evaporated onto various single crystal substrates at a base pressure of 10^{-10} torr. Different surface-supported structures were imaged via STM at sub-molecular resolution, allowing the competition of molecule-substrate and molecule-molecule interactions to be investigated.

In addition to imaging via STM, we also performed spectroscopy experiments in the forms of UHV Tip Enhanced Raman Spectroscopy (TERS), supplementing vital vibrational information at single-molecule spatial resolution. These tools provide a complete picture of the system in question, allowing our lab to answer previously unknown questions regarding the molecule-molecule interactions in order to characterize the molecule’s exciton-generating and electron-transferring properties at a fundamental level.

8:20am **NS+AS+EM+MI+SP+SS-ThM2 BCC to FCC Phase Transition of Pd_xCu_{1-x} at Nanoscale**, ***Xiaoxiao Yu***, Carnegie Mellon University, *A. Gellman*, Carnegie Mellon University, W.E. Scott Institute for Energy Innovation

One of the most interesting characteristics of alloy nanoparticles (NPs) is that they can have different phases from those of the bulk. In the bulk phase diagram of Pd_xCu_{1-x}, there exists a composition range, $0.35 < x < 0.55$, over which a B2 phase (ordered body centered cubic, CsCl structure) is formed at T < 873 K, in spite of the fact that pure Pd and Cu both have face centered cubic (FCC) bulk crystal structures. An experimental methodology has been developed for determining the phase behavior of Pd_xCu_{1-x} size and composition spread nanoparticle (SCSNP) libraries. Spatially resolved X-ray photoemission spectroscopy (XPS) was used to map the Cu $2p_{3/2}$ core level shifts (CLS) with respect to the value for pure Cu across composition space on the bulk Pd_xCu_{1-x} alloy. The result has shown that the Cu $2p_{3/2}$ binding energy decreases monotonically with increasing Pd at.% in the FCC phase. There is additional discontinuous CLS over the composition range from 0.35 to 0.55 Pd at.%, where the B2 phase forms. Therefore, the Cu $2p_{3/2}$ core level binding energy measured by XPS can be used to distinguish between the ordered B2 phase and disordered FCC phase. The Pd_xCu_{1-x} SCSNP library on a Mo substrate was prepared using a rotatable shadow mask deposition tool previously developed by our group. After annealing the Pd_xCu_{1-x} alloy thin film to 700 K, the additional CLS over the composition range, $0.35 < x < 0.55$, has been observed at a film thickness > 6 nm, which suggests the formation of B2 phase. However, at a film thickness between 4 – 6 nm, the Cu $2p_{3/2}$ binding energy decreases monotonically across composition space which suggests that only FCC phase exists for alloy films in this thickness range. Because the FCC phase is more densely packed than the B2 phase, the surface tension in this thickness regime can drive a conversion from the ordered B2 phase back to the randomly distributed FCC solid solution. More interestingly, the additional CLS over the composition range from 0.35 to 0.55 Pd at.% reoccurs at a film thickness < 4 nm, which suggests the formation of B2 phase. This observation is the result of dewetting of the Pd_xCu_{1-x} NPs after heating at 700 K for 30 mins, and the size of dewetting NPs exceeds 6 nm where the close-packed FCC phase is stabilized. Dewetting of Pd_xCu_{1-x} NPs is validated by the appearance of the substrate Mo XPS signal at a film thickness < 4 nm. This comprehensive experimental study of the phase behavior for Pd_xCu_{1-x} alloy NPs will be correlated with their catalytic activity across composition and size spaces to accelerate the development of alloy NPs for catalytic applications.

8:40am **NS+AS+EM+MI+SP+SS-ThM3 Hybrid Environmental Transmission Electron Microscope: An Integrated Platform for In situ Imaging and Spectroscopies**, ***Renu Sharma***, NIST **INVITED**

Environmental transmission electron microscopes (ETEM) and TEM holders with windowed reaction cells, enable in situ measurements of the dynamic changes occurring during gas-solid and/or liquid-solid interactions. The combination of atomic-resolution images and high spatial and energy resolution has successfully revealed the nucleation and growth mechanisms for nanoparticles, nanowires, carbon nanotubes and the functioning of catalyst nanoparticles. While TEM-based techniques are ideally suited to distinguish between active and inactive catalyst particles and identify active surfaces for gas adsorption, we still must answer the following questions: (1) Are our observations, made from an area a few hundred nanometers in extent, sufficiently representative to determine the mechanism for a specific reaction? (2) Is the reaction initiated by the incident electron beam? (3) Can we determine the sample temperature accurately enough to extract quantitative kinetic information? And (4), can we find efficient ways to make atomic-scale measurements from the thousands of images collected using a high-speed camera. The lack of global information available from TEM measurements is generally compensated by using other, ensemble measurement techniques such as x-ray or neutron diffraction, x-ray photoelectron spectroscopy, infrared spectroscopy, Raman spectroscopy etc. However, it is almost impossible to create identical experimental conditions in two separate instruments to make measurements that can be directly compared.

We have designed and built a unique platform that allows us to concurrently measure atomic-scale and micro-scale changes occurring in samples subjected to identical reactive environmental conditions by incorporating a Raman Spectrometer into the ESTEM. We have used this correlative microscopy platform i) to measure the temperature from a 60 μm^2 area using Raman shifts, ii) to investigate light/matter interactions in plasmonic particles iii) to act as a heating source, iii) to perform concurrent optical and electron spectroscopies such as cathodoluminescence, electron energy-loss spectroscopy and Raman. We have developed an automatic image-processing scheme to measure atomic positions, within 0.015 nm uncertainty, from high-resolution images, to follow dynamic structural changes using a combination of algorithms publicly available and developed at NIST. This method has been proven to capture the crystal structure fluctuations in a catalyst nanoparticle during growth of single-walled carbon nanotube (SWCNT). Details of the design, function, and capabilities of the optical spectrum collection platform and image processing scheme will be presented.

9:20am **NS+AS+EM+MI+SP+SS-ThM5 Critical Dimension Metrology by Localization Optical Microscopy**, *C.R. Copeland, C.D. McGray, J.C. Geist, J.A. Liddle, B.R. Ilic, **Samuel Stavis***, NIST

Optical microscopy methods of localizing subresolution emitters are broadly useful in many fields from biology to nanofabrication. Precision and accuracy are fundamental for localization measurements. Subnanometer precision is readily achievable for many emitters and can elucidate structure and motion at atomic scales, but is potentially false precision in the absence of calibrations that enable corresponding accuracy, particularly over a wide field for imaging and tracking. Whereas improving localization precision generally requires counting more photons by increasing emitter intensity and stability, improving localization accuracy presents diverse challenges in the calibration of an optical microscope as a measurement system. This involves not only its discrete components but also their interaction during a measurement. Such calibration is complex, motivating the development of practical devices and methods to facilitate the process, which we present here.

First, we characterize a complementary metal oxide semiconductor (CMOS) camera, enabling full use of its dynamic range and megapixel array. Next, we fabricate aperture arrays by electron-beam lithography and test them as calibration devices, exploiting their uniformity and stability. Then, we refine localization analysis, presenting a novel estimator and accommodating saturation. Finally, we evaluate aberrations of our optical system, including field curvature, distortion, and others that break the symmetry of the point spread function. After calibrating our system in this way, we validate our widefield measurements and demonstrate critical dimension localization microscopy (CDLM) of aperture arrays, and answer open questions about the apparent motion of nanoparticle fiducials. Our study casts new light on localization microscopy at subnanometer scales.

Our study also highlights the importance of nanoscale fabrication and metrology in achieving localization accuracy. Previous studies have applied aperture arrays for lens evaluation but have not quantified their critical dimensions, in particular the array pitch. This is essential to ensure that electron-optical aberrations do not propagate as errors through the calibration and correction of photon-optical aberrations. Moreover, the application of CDLM to aperture arrays provides useful information on the effects of dose delivery and beam scanning to optimize the future nanofabrication of reference materials.

9:40am **NS+AS+EM+MI+SP+SS-ThM6 Tunable Emission from Nanophotonic Structures in a Modified SEM: Characterizing Smith Purcell Radiation Generation from the VUV to the Near IR**

__Steven Kooi__, I. Kaminer, A. Massuda, M. Soljačić, C. Roques-Carmes, MIT

We present theoretical predictions and experimental results of multiple order Smith-Purcell radiation in a variety of samples from periodic high aspect ratio silicon nanowire structures to engineered metasurfaces using low-energy electrons (2.5 -20 keV) in a modified scanning electron microscope. The samples emit photons in a controlled way and we demonstrate optical emission from the VUV to the near IR, opening a pathway to building a fully tunable optical source that we intend to extend into the soft X-Ray regime.

11:00am **NS+AS+EM+MI+SP+SS-ThM10 Ultrafast Optical Response of Graphene/LaAlO$_3$/SrTiO$_3$ Heterostructure**

L. Chen, E. Sutton, J. Li, M. Huang, J.F. Hsu, B. D'Urso, University of Pittsburgh, *J.W. Lee, H. Lee, C.B. Eom,* University of Wisconsin-Madison, *P. Irvin, __Jeremy Levy__*, University of Pittsburgh **INVITED**

The unique electronic and optical properties of graphene make it a promising device in terahertz(THz) regime. Another 2D electron system, the complex-oxide heterostructure LaAlO$_3$/SrTiO$_3$, has been shown to exhibit great promise for control and detection of broadband THz emission at extreme nanoscale dimensions[1]. Recently, we have successfully integrated these two platforms: we have created graphene/LaAlO$_3$/SrTiO$_3$ structures with (1) high mobility in the graphene channel[2] and (2) oxide nanostructures patterned directly underneath the graphene layer[3]. Here we describe new experiments that probe graphene with this nanoscale THz spectrometer using ultrafast optical techniques. This unprecedented control of THz radiation at 10 nm length scales creates a pathway toward hybrid THz functionality in graphene/LaAlO$_3$/SrTiO$_3$ heterostructures.

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11:40am **NS+AS+EM+MI+SP+SS-ThM12 Single-Molecules Fluorescence Spectroscopy and Lifetime with Simultaneous Super-resolution Imaging for Materials Science Applications**

__James Marr__, CNST/NIST and University of Maryland, *M. Davanço,* CNST/NIST, *S.J. Stranick,* NIST, *B.R. Ilic, J.A. Liddle*, CNST/NIST

We have developed a widefield imaging system that measures single-molecule position, orientation, lifetime and fluorescence spectra. We achieve this by combining conventional super-resolution imaging using an sCMOS detector with a unique, photon-counting, wide-field, high-temporal, high-spatial resolution, high-throughput, three-dimensional detector (H33D). The use of dual-objectives maximizes the fluorescent photon flux to each camera. Individual fluorophore point-spread functions collected by the sCMOS detector provide position and orientation information, while the 100 ps timing resolution of the H33D detector enables us to make precise lifetime measurements of the same fluorophore. By incorporating a diffraction grating into the beam path of the sCMOS camera we can simultaneously record both a zero-order image of each fluorophore for position and orientation measurement, and a wavelength-dispersed image that provides single-molecule spectroscopic data. The sensitivity of fluorophore lifetime, spectroscopic behavior, orientation, and position to dynamic processes in soft materials with nanosecond, millisecond, and second timescales, respectively, enables us to collect three-dimensional, local structure-property information that would otherwise be impossible to obtain. We have fabricated unique structures that enable us to accurately determine the influence of metallic and high-refractive index materials on fluorophore lifetime and point-spread function shape. Our far-field system, combined with these nanoengineered structures, permit minimally-perturbative measurements to be made on individual fluorophores. We apply our imaging system to probe the nanoscale behavior of polymers in nanocomposite materials and to investigate fluorophore response to structured samples consisting of thin, high-refractive index materials.

12:00pm **NS+AS+EM+MI+SP+SS-ThM13 Atomic Scale Surface Effects of Controlled Crystal Structure in III-V Semiconductor Nanowires: Preferential Surface Alloying and Local Electronic Properties.**

J. Knutsson, M. Hjort, Lund University, Sweden, *P. Kratzer,* University Duisburg-Essen, Germany, *J. Webb, S. Lehmann, K.D. Thelander,* Lund University, Sweden, *C.J. Palmstrom,* UCSB, *R. Timm, __Anders Mikkelsen__*, Lund University, Sweden

Despite the many III-V nanowire (NW) technologies under current development, be it solar cells and light emitting diodes or high speed/low power electronics, there are still only few studies of their surfaces. The atomic scale structure and morphology of NW surfaces are however central in determining their functionality, due to the inherently large surface to bulk ratio. In addition, III-V NWs can be tailored with segments of both the cubic zinc blende (ZB) and hexagonal wurtzite (WZ) structures and in a variety of materials combinations. This allow experimental access to nanocrystallite surfaces and interfaces not found in the bulk. We have demonstrated atomically resolved Scanning Tunneling Microscopy/Spectroscopy (STM/S) on a wide variety of these III-V NWs and on operational NW devices [1-5]. We now use these methods for studying atomic scale surface structural changes and impact on local electronic properties on both GaAs and InAs NWs at room temperature and at 5K.

We explore the surface diffusion and alloying of Sb into GaAs NWs with controlled axial stacking of Wz and Zb crystal phases. We find that Sb preferentially incorporates into the surface layer of the -terminated Zb segments rather than the -terminated Wz segments. Density functional theory calculations verify the higher surface incorporation rate into the Zb phase and find that it is related to differences in the energy barrier of the Sb-for-As exchange reaction on the two surfaces. These findings demonstrate a simple processing-free route to compositional engineering at the monolayer level along NWs.

Using low temperature STM/S we measure local density of states of atomic scale tailored Zb segments in Wz InAs nanowires down to the smallest possible crystal lattice change. We find that Zb crystal phase signatures can be seen in the density of states both on the conduction and valence band sides as well as in the band positions down to the smallest possible Zb segment. Additionally we find indications of confined state effects due to the difference in bandgap between Wz and Zb. Finally we explore the stability of InAs NWs with atomic scale STM during the application of voltages through the NWs in a device configuration. We observe that applying realistic voltages to InAs NWs results in removal of atomic scale defects and smoothening of the morphology.

[1] E. Hilner et al., Nano Letters, 8 (2008) 3978; M. Hjort et al., ACS Nano 6, 9679 (2012)

[2] M. Hjort et al., Nano Letters, 13, 4492 (2013)

[3] M. Hjort et al., ACS Nano, 8 (2014) 12346

[4] J. L. Webb, et al Nano Letters 15 (2015) 4865

[5] J. L. Webb et al., Nano Research, 7 (2014) 877

[6] O. Persson et al., Nano Letters 15 (2015) 3684

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room: 9 - Session SA+AC+MI-ThM

Frontiers in Probing Properties and Dynamics of Nanostructures and Correlation Spectroscopy
Moderators: Jan Vogel, Institut Néel, CNRS/UGA, Grenoble, France, Christian Gutt, University of Siegen, Germany

8:00am **SA+AC+MI-ThM1 X-rays Revealing Exotic Properties of Magnetoelectric Multiferroics and Related Materials**, ***Elke Arenholz***, Lawrence Berkeley National Laboratory **INVITED**

Engineering novel materials with structural, electronic and/or magnetic characteristics beyond what is found in bulk systems is possible today through the technique of thin film epitaxy, effectively a method of 'spray painting' atoms on single crystalline substrates to create precisely customized thin films or layered structures with atomic arrangements defined by the underlying substrate. The abrupt change of composition at as well as charge and spin transfer across interfaces can also lead to intriguing and important new phenomena testing our understanding of basic physics and creating new functionalities.

We use soft x-ray spectroscopy and scattering to probe and understand the electronic, magnetic and structural characteristics of novel engineered materials such as magnetoelectric multiferroics, i.e. materials that exhibit simultaneous order in their electric and magnetic ground states. These materials hold promise for use in next-generation memory devices in which electric fields control magnetism but are exceedingly rare in bulk form. Engineering magnetoelectric multiferroics by interleaving two or more atomically thin layers is an intriguing new approach. A very recent example is establishing room temperature coexisting ferromagnetic and ferroelectric order in $LuFeO_3)_m/(LuFe_2O_4)_1$ superlattices. [1] We used soft x-ray spectroscopy and microscopy to characterize the magnetic order and ferroelectric polarization of the system.

Similarly intriguing is engineering the orbital symmetry of emergent quantum states near the Fermi edge at interfaces determining the mobility of interfacial conduction electrons in novel heterostructures. Using soft x-ray linear dichroism (XLD), we investigated the orbital stares of interfacial electrons in $Al_2O_3/SrTiO_3$ and developed an interesting route to engineer emergent quantum states with deterministic orbital symmetry [2].

[1] J. A. Mundy *et al*., Nature **537**, 523 (2016).

[2] Y. Cao *et al*., npj Quantum Materials **1**, 16009 (2016).

8:40am **SA+AC+MI-ThM3 X-ray Reflectivity Investigations of Ultrafast Dynamics in Magnetic Multilayer Structures**, ***Christian Gutt***, *T. Sant, D. Ksenzov, U. Pietsch,* University of Siegen, Germany, *J. Luening,* Sorbonne University, *F. Capotondi, E Pedersoli, M. Manfredda, M. Kiskinova,* Elettra-Sincrotrone Trieste, Italy, *M. Klaeui, H. Zabel,* University of Mainz **INVITED**

Exciting a ferromagnetic material with an ultrashort IR laser pulse is known to induce a reduction of magnetic order and ultrafast spin diffusion processes . Both processes produce disorder on 100s fs scales and their role in a deterministic creation and switching of magnetic order is still poorly understood. Here, we demonstrate that a nanoscale magnetization-reversal exists in the vicinity of domain walls in the near-surface region of a ferromagnetic Co/Pd thin film upon IR excitation. This magnetization-reversal is driven by the different transport properties of majority and minority carriers through a magnetically disordered domain network. We followed the ultrafast temporal evolution by means of an ultrafast resonant magnetic scattering experiment in surface scattering geometry, which enables to exploit the domain network within the top 3 nm to 5 nm layers of the FM film. We observed magnetization-reversal close to the domain wall boundaries that becomes more pronounced moving closer to the film surface. Its lateral extension has allowed us to measure the ultrafast spin-diffusion coefficients and ultrafast spin velocities for majority and minority carriers upon IR excitation.

9:20am **SA+AC+MI-ThM5 Spray Deposition of Water-processed Active Layers of Hybrid Solar Cells Investigated with In situ X-ray Scattering Methods**, ***Volker Körstgens***, *F. Buschek, M. Wörle,* Technische Universität München, Germany, *W. Ohm,* DESY, Germany, *H. Iglev,* Technische Universität München, Germany, *S.V. Roth,* DESY, Germany, *R. Kienberger, P. Müller-Buschbaum,* Technische Universität München, Germany

In the development of non-conventional solar cells not only the achievements of highest power conversion efficiencies and maximum lifetime of devices is of interest. Also the sustainability of the production process of the devices comes into focus. In order to achieve an all-embracing green technology, the materials applied and the required energy for device fabrication are of importance. Materials in terms of functional components or as additives in the processing should be non-toxic and environmentally friendly. In an optimum approach no organic solvents should be used for the coating of any of the layers of the corresponding devices. High temperature processing steps should be reduced or avoided to increase the energy payback times of the solar cells. Following this idea, we developed hybrid solar cells with an active layer based on low temperature processed titania and a water-soluble polymer [1]. In our approach titania nanoparticles are produced with laser ablation in liquid in order to initiate a functionalization of titania with the polymer for the active layer. Combining these titania nanoparticles and water-soluble poly[3-(potassium-6-hexanoate)thiophene-2,5-diyl] (P3P6T) hybrid solar cells are realized. In order to improve conversion efficiencies of these devices a vertical compositional gradient of the two components of the active layer was introduced. For the fabrication of hybrid photovoltaic devices we applied spray-coating as the deposition method for the active layer which could easily scale-up to industrial cost-effective fabrication. For the deposition of the active layer with laser-ablated particles spray deposition provides a good control of the film thickness. The morphology of the active layer is of major importance for the performance of hybrid solar cells. We are especially interested in how the morphology changes with ongoing deposition process. Therefore we followed the development of the morphology of the active layer in situ with high spatial and temporal resolution. The mesoscale was probed with in situ GISAXS, whereas the crystallinity of the polymer and the inorganic component was investigated with in situ GIWAXS. The changes of the morphology and the influence on photovoltaic performance with the introduction of a compositional gradient are discussed. As the synchrotron-based investigation allowed for a high temporal resolution of 0.1 s, insights into the very first stages of the deposition process were obtained. From the overall situ study improvements for the spray deposition procedure are derived that allow for a better control of the morphology of the devices.

[1] Körstgens et al., Nanoscale 7, 2900 (2015)

9:40am **SA+AC+MI-ThM6 New Instrumentation for Spin-integrated and Spin-resolved Momentum Microscopy – METIS and KREIOS**, ***Thomas Schulmeyer***, *M. Wietstruk, A. Thissen,* SPECS Surface Nano Analysis GmbH, Germany, *G. Schoenhense,* Johannes Gutenberg-Universität, Germany, *A. Oelsner,* Surface Concept GmbH, Germany, *C. Tusche,* Max Planck Institute for Microstructure Physics, Germany

Two new momentum microscopes are presented by SPECS: our newly developed time-of-flight momentum microscope METIS and the energy dispersive and filtered momentum microscope KREIOS. Both are using an optimized lens design which provides simultaneously highest energy, angular and lateral resolution. The lens provides a full 2π 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. Operation modes are (k_x,k_y,E_k) data acquisition by operation in energy filtered k-space imaging, (ToF-)PEEM mode, energy-filtered real space imaging and micro-spectroscopy mode.

The 3D (k_x, k_y, E_k) data recording is done with a 2-dimensional delayline detector, with a time resolution of 150 ps and count rates up to 8 Mcps. It uses channelplates with 40 µm spatial resolution. While the x,y position of an incoming electron is converted into k_x,k_y wave vector, the kinetic energy E_k is determined from the flight time t in METIS or obtained directly by the energy filter in KREIOS. Spin-resolved imaging is achieved by electron reflection at a W(100) spin-filter crystal prior to the 2-dimensional delayline detector. Electrons are reflected in the [010] azimuth at 45° reflection angle. Varying the scattering energy one can choose positive, negative, or vanishing reflection asymmetry.

Besides a description on how the instruments work data from both instruments on different single crystalline materials will be presented.

11:00am **SA+AC+MI-ThM10 X-ray Photon Correlation Spectroscopy Studies of Soft Matter and Biomaterials**, ***Laurence B. Lurio***, Northern Illinois University **INVITED**

The use of x-ray photon correlation spectroscopy to study dynamics in soft materials and bio-materials will be reviewed. Examples will be presented from the dynamics of colloidal suspensions, polymers and concentrated proteins.

11:40am **SA+AC+MI-ThM12 Forefront Applications of XPCS**, ***Anders Madsen***, European XFEL GmbH, Germany **INVITED**

Recent advances in dynamics studies of condensed matter by X-ray photon correlation methods will be discussed. Classical X-ray Photon Correlation Spectroscopy (XPCS) requires a (partially) coherent beam and a reliable detector and has benefitted a lot from recent synchrotron source upgrades and the advent of novel 2D pixel detectors. Weakly scattering systems and fast dynamics can now be characterized much better than only a few years back. The next generation of X-ray sources - X-ray Free-Electron Lasers (XFEL) - will deliver many orders of magnitude more coherent intensity than the present generation of synchrotrons but at the same time the pulsed nature of XFELs requires new XPCS-like techniques to be developed. In the presentation I discuss a few new methods that take advantage of the XFEL pulse pattern and allow dealing with the pertinent problem of beam induced damage to the samples. Examples of Scientific applications in soft- and hard-condensed matter will be given as well as an outlook to the forthcoming European XFEL facility where time-resolved coherent X-ray experiments will be carried out at the MID station.

Surface Science Division
Room: 25 - Session SS+EM+HC+MI-ThM

Oxides: Structures and Reactions

Moderators: Valeria Lauter, Oak Ridge National Laboratory, Charles Sykes, Tufts University

8:00am **SS+EM+HC+MI-ThM1 Influence of Iron Doping on Cobalt Oxide Bilayers on Au(111): Toward a Model of Synergistic Catalytic Effect in Oxygen Evolution Reaction**, ***Jonathan Rodriguez-Fernandez***, *Z. Sun, J. Fester, J.V. Lauritsen*, Aarhus University, Denmark

Iron doped cobalt oxides have been shown enhanced activity for promoting the oxygen evolution reaction (OER) compared with unary iron oxides and cobalt oxides, respectively[1]. However, the nature of such synergistic catalytic effect and in particular the way of iron species incorporate with cobalt oxides are only understood on a superficial level, which presents a significant obstacle to further exploration on rational design of efficient OER catalysts. Noble metal supported transition metal oxides have been previously applied as model catalysts, which enables the powerful surface science techniques, and successfully reveal the catalytic active sites and help researchers understand the catalytic process further[2].

Here, aiming to study the origin of the synergistic catalytic effect, we dope iron into well-characterized cobalt oxide bilayer nanoislands supported on a single crystal Au(111) substrate[3]. Atomic-resolved scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) are used to compare the growth of cobalt oxide and cobalt-iron oxide bilayers. We perform a comprehensive analysis of the iron doping induced influence on the atomic structure of the nanoislands and oxidation states of both the dopant and host species.

We find that doped iron species integrate into the cobalt oxide nanoislands and are mostly under oxidative condition. The Co atoms surrounding the doped Fe appear brighter and form 6-fold flower-like features under STM due to the local modification of electronic structure, which indicates changed chemical activities of these atoms. Similar situation happens on O atoms near doped Fe and form 3-fold triangle-like features. XPS spectra imply that Co keeps 2+ oxidation state whereas Fe shows 3+ oxidation state, which is not the same with the oxidation state of 2+ in the iron oxide nanoislands, indicating that iron species in the cobalt-iron oxides have stronger oxidizing ability. Further water exposure experiments demonstrate that hydroxyl groups usually appear next to the doped iron sites while almost randomly distributed on the basal plane of pure cobalt oxide nanoislands, suggesting that iron species in the cobalt-iron oxide play an important role in promoting the catalytic activity.

References

1. Burke, Michaela S., et al., Journal of the American Chemical Society 137.10 (2015): 3638-3648.

2. Fester, J., et al., Nature Communications 8 (2017): 14169.

3. Walton, Alex S., et al., ACS Nano 9.3 (2015): 2445-2453.

8:20am **SS+EM+HC+MI-ThM2 An Ordered Mixed Oxide Monolayer formed by Iron Segregation on Rutile-TiO_2(011)**, ***Sandamali Halpegamage***, University of South Florida, *L. Bignardi, P. Lacovig*, Elettra-Sincrotrone Trieste, Italy, *A. Kramer*, University of South Florida, *Z. Wen, X. Gong*, East China University of Science and Technology, PR China, *S. Lizzit*, Elettra-Sincrotrone Trieste, Italy, *M. Batzill*, University of South Florida

Ternary oxide monolayers supported on or intermixed with a second oxide surface have attracted great interest in designing new materials with unique chemical functional properties including selective heterogeneous catalysts and nanocatalysts. Due to the complexity of the structure and composition, it is challenging to discover and characterize such phases. Here we synthesized an ordered mixed oxide monolayer of $FeTi_2O_5$ on rutile-TiO_2(011) via two different experimental pathways; firstly, by annealing the clean TiO_2(011) in $1x10^{-7}$ mbar of O_2 at ~450 ^{0}C and secondly, by physical vapor depositing Fe on clean TiO_2(011) in $1x10^{-7}$ mbar of O_2 at ~450 ^{0}C.In both procedures the Fe atoms intermixe with Ti atoms in the surface layer of the substrate and form an ordered mixed-oxide monolayer with $FeTi_2O_5$ composition. High resolution and fast X-ray photoemission spectroscopy (XPS) reveals that Fe and Ti are in 2+ and 4+ charge states respectively. The structure of this mixed oxide monolayer was predicted by a combination of atomically-resolved STM (Scanning Tunneling Microscopy) and DFT-based calculations and further confirmed by synchrotron based angle scanned x-ray photoelectron diffraction (XPD) studies. Multiple electron scattering simulations implemented in the Electron Diffraction in Atomic Clusters (EDAC) package were performed for comparing experimental XPD patterns with structural models. Judged by the reliability factor (R_p), the experimentally determined XPD patterns are in good agreement with the simulated XPD patterns. The study has been extended to a few of the other transition metals namely, V, Cr, and Ni. Due to the similarities in the bulk oxide structures of these transition metals they all are capable of forming similar intermixed monolayer oxide surfaces with the composition MTi_2O_5 (M=V,Ni,Cr). For all these monolayers, the valance band maximum (VBM) is above the VBM for TiO_2, suggesting that these monolayers may trap holes at the surface efficiently and thus may modify the photocatalytic activity of TiO_2.

8:40am **SS+EM+HC+MI-ThM3 Growth and Chemistry of rutile IrO_2 Surfaces**, ***Jason Weaver***, *Z. Liang, T. Li, R. Rai*, University of Florida, Gainesville, *M. Kim, A. Asthagiri*, The Ohio State University **INVITED**

Interest in the surface chemistry of late transition-metal oxides has been stimulated by observations that the formation of metal oxide layers tends to dramatically alter the catalytic performance of transition metals in applications of oxidation catalysis. In this talk, I will discuss our recent investigations of the growth and chemical properties of rutile IrO_2 surfaces. I will discuss our studies of the oxidation of metallic Ir surfaces by O-atom beams as well as O_2 at pressures above 1 Torr. We find that stoichiometrically-terminated IrO_2(110) layers could only be formed by oxidizing Ir(111) and Ir(100) at sufficiently high temperature and O_2 pressure. I will discuss the binding characteristics of small molecules, and our recent discovery of highly facile CH_4 activation on the IrO_2(110) surface at temperatures as low as 150 K.

9:20am **SS+EM+HC+MI-ThM5 Formation and Manipulation of Water Clusters on Bilayer ZnO Surface**, ***Junseok Lee***, *D.C. Sorescu, X. Deng*, National Energy Technology Laboratory

Adsorption of water on the nanostructured metal oxide surfaces has implications in catalysis and serves as a prototypical system in studying water-oxide interfaces. By using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, the clustering behavior of water on the bilayer ZnO surface grown on Au(111) has been studied at low coverage regime. Diffusion and clustering of water molecules at specific sites in the Moire pattern are observed after initial adsorption of water on bilayer ZnO at T = 77 K. Heating the surface to T < ~240 K reveals that the adsorbed water molecules form triangular shape clusters with two specific orientations in the STM images. The DFT calculations along with the experimental findings suggest that the clusters are comprised of mixed water and hydroxyl groups with a binding energy of 21 kcal/mol. The two types of clusters can be converted to each other by the injection of electron from the STM tip. The inelastic electron scattering process is considered to be responsible for the conversion of the clusters via O-H stretch vibration mode excitation.

9:40am **SS+EM+HC+MI-ThM6 Formation of Metastable Water Chains on Anatase TiO_2(101)**, ***Arjun Dahal***, *Z. Dohnálek*, Pacific Northwest National Laboratory

The interaction of water with metal oxide surfaces is of great importance in many diverse areas such as catalysis, electrochemistry, corrosion, atmospheric science, geology, astrophysics, and others. Anatase TiO_2 surface is particularly relevant because it is the most active polymorph of TiO_2 and its commercially employed nanomaterials grow preferentially as anatase. In this study, we employ scanning tunneling microscopy (STM) to study the adsorption of water on a model stoichiometric anatase TiO_2(101) surface.

Well-defined anatase TiO_2(101) surface has saw-tooth-like morphology exposing alternating rows of two-fold-coordinated oxygen atoms (O_{2c}) and five-fold-coordinated Ti atoms (Ti_{5c}) along the [010] direction. Our STM data show that at 80 K isolated water monomers bind molecularly to the Ti_{5c} sites. The onset of diffusion is found at ~190 K where water monomers diffuse both along and across the Ti_{5c} rows. The analysis shows that the along-the-row diffusion is energetically favored by only 0.03 eV. Surprisingly, we find that at 80 K water molecules start to form linear chains along the Ti_{5c} rows as the coverage is increased. This indicates the presence of transient mobility of water molecules suggesting that the adsorption occurs via a precursor state. When the water chains are annealed at 190 K, they fall apart to monomers that reside on the next-nearest-neighbor Ti_{5c} sites. These results demonstrate that the water chains are metastable in nature. This is at odds with many other oxide surfaces where hydrogen-bonded water clusters are energetically preferred over the isolated monomers.

11:00am **SS+EM+HC+MI-ThM10 The Structure of Fe_2O_3(012) and its Reactivity to Water**

***Gareth Parkinson**, F. Kraushofer, Z. Jakub, M. Bichler, J. Hulva, M. Schmid, U. Diebold, P. Blaha*, TU Wien, Austria

Hematite (α-Fe_2O_3) is a promising material for technological applications due to its abundance, low cost and chemical stability. Its 2.2 eV bandgap makes it potentially ideal as a photoanode for photoelectrochemical water splitting, [1] but performance is hampered by slow reaction kinetics and the need for a significant overpotential. Little is known about the atomic-scale structure of hematite surfaces, and even less about how this relates to photocatalytic activity.

To date, most surface science studies of α-Fe_2O_3 have focused on the (001) facet, but preparing a stoichiometric surface under UHV conditions has proven problematic. Some authors have investigated the equally relevant (012) surface, [2][3][4] and reported that a (1x1) and a reduced (2x1) termination can be reversibly prepared. Several models have been proposed for the (2x1) reconstruction, but as yet no scanning probe data exists to support or refute them.

Here we present a multi-technique study of the (1x1) and (2x1) surfaces of α-Fe_2O_3 (012), as well as their interaction with water. The data acquired for the (1x1) termination support a bulk termination model, as predicted by previous publications, but STM and nc-AFM images of the (2x1) reconstruction are inconsistent with previously proposed models. [3] We propose a new model based on ordered oxygen vacancies, the plausibility of which is confirmed by density functional theory (DFT) results. TPD and XPS data reveal that the (1x1) surface adsorbs water in a mixed-mode fashion, whereas the interaction with the (2x1) surface is entirely dissociative. We propose models for the structure of the adsorbed overlayers based on scanning probe microscopy data.

References

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[3] Henderson, M. A. *Surface science* **515**, 253-262 (2002).

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11:20am **SS+EM+HC+MI-ThM11 Interaction of Water with anatase TiO_2(001)-1x4**

***Igor Beinik**, K.C. Adamsen, S. Koust, J.V. Lauritsen, S. Wendt*, Aarhus University, Denmark

The interaction of water with titanium dioxide (TiO_2) is pivotal for many practical applications of this material in heterogeneous catalysis because water is almost always present either as a reactant or a product in many catalytic reactions. In our model study, we focus on the anatase polymorph of TiO_2 that has demonstrated a higher catalytic activity in water splitting than rutile and is generally considered as a more technologically relevant polymorph. The nanocrystals of anatase that are present in powder catalysts normally expose a high fraction of low surface energy (101) facets and a significantly smaller fraction of high energy, but supposedly more reactive (001) facets. The (001) facet is intrinsically unstable and reconstructs upon annealing in vacuum forming 1x4 reconstructed terraces, where rows of bridging oxygen atoms in [100] and [010] directions are replaced by TiO_3 units [1]. This kind of reconstruction has been found both on the (001) facets of anatase single crystals and nanoparticles [2], however the interaction of water with this surface has been significantly less investigated.

In the present work, we study the adsorption and dissociation of water on the anatase (001) 1x4 reconstructed surface by means of STM, TPD, and synchrotron core-level and valence band PES under UHV conditions. Our results show that water dissociates to some extent even at 120 K and that low water exposures (up to 3 L) at this temperature results in a mixture of molecularly and dissociatively adsorbed molecules. A systematic analysis of the data obtained using all three techniques leads us to a conclusion that the A-TiO2(001)-1x4 surface is rather reactive - in agreement with an earlier study [3] we find that water dissociates at the ridges of the 1x4 reconstruction. Moreover, the 1x4 reconstruction remains stable upon water exposures at least up to ~45 L (at 120 K). However, after desorption of a multilayer ice film, the ridges themselves contain a high number of defects, which remain stable up to 800 K. The nature of these defects will be discussed.

References:

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3. Blomquist, J., et al. J Phys Chem C **112**, 16616–16621 (2008).

Thin Films Division
Room: 21 - Session TF+MI+NS-ThA

ALD and Nanostructures
Moderators: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, France, Richard Vanfleet, Brigham Young University

2:20pm **TF+MI+NS-ThA1 Coating and Infilling 3D Geometries by Low-T CVD : HfB_2 throughout 0.5 mm Thick CNT Forests**, ***John Abelson***, University of Illinois at Urbana-Champaign **INVITED**

We describe the use of extremely conformal chemical vapor deposition to coat carbon nanotube forests throughout their depth with a film of HfB_2, a mechanically hard, electrically conductive and highly refractory alloy. CVD uses the precursor $Hf(BH_4)_4$ at partial pressures ≤ 15 Torr at substrate temperatures ≤ 200°C. The CNT forests are up to 500 µm thick and can be shaped by pre-depositing patterns of seed metal on the underlying substrate prior to their synthesis.

Coating CNT forests affords a new class of composite foams with adjustable mechanical properties : the HfB_2 coating both stiffens individual tubes and "welds" them together wherever they touch, whereas in the uncoated forest the tubes can slide relative to one another. We fabricate cylindrical pillar structures with HfB_2 thicknesses from 3-50 nm. As measured by nanoindentation using a flat punch, the Young's modulus varies over three orders of magnitude as $E \sim \rho^{1.7}$, where the mass density ρ is dominated by the HfB_2 coating. The maximum stiffness and strength are 56 and 1.9 GPa, respectively.

A major question is how CVD can achieve a nearly uniform coating in such a deep structure. The challenge is inherent in the diffusion-reaction kinetics : the transport of reactants occurs by molecular diffusion, which is slow in narrow cross-sections; while at the same time the reaction (consumption) rate must be high enough to be useful. In combination, these factors imply that the partial pressure (flux) of reactants must diminish with depth; if the film growth rate varies monotonically with flux, then the coating thickness must decline with depth in the structure.

The solution is to (i) employ a precursor that exhibits a hard saturation in the growth rate vs. partial pressure, (ii) use a high partial pressure above the sample, and (iii) grow at low temperature to limit the reaction rate. Under these conditions, even though the partial pressure of precursor drops considerably from the top to the bottom of the sample, the growth rate remains almost constant. To achieve the high precursor pressure, we employ a static (unpumped) reaction tube apparatus. We previously derived a master relationship [1] that predicts the precursor pressure (p) necessary to achieve a desired step coverage (SC) and growth rate (GR) in a given aspect ratio (AR) given knowledge of the atomic density (r), growth rate coefficient (K) and molecular diffusivity (D_0): $p = (GR\ AR) * ((c\ r\ kT) / (2\ D\ K) * (1 - SC))$^0.5

We will discuss extension of this method to other thin film systems and substrate geometries.

1. A. Yanguas-Gil, Y. Yang, N. Kumar, and J. R. Abelson, JVST A **27,** 1235 (2009) [DOI: 10.1116/1.3207745]

3:00pm **TF+MI+NS-ThA3 Varying Penetration Depths in ALD on High Aspect Ratio Carbon Nanotube Forests**, ***David Kane***, *RC. Kane, R.R. Vanfleet*, Brigham Young University

We have observed steps in the penetration depth in atomic layer deposition on tall vertically aligned multiwall carbon nanotube (MWCNT) forests. The deposition thickness at the top of the forest is greater than that at the bottom and varies in distinct steps. The MWCNT forests used were 200 µm tall with an aspect ratio of about 2000. In the thermal TMA/water process on MWCNTs, precursor pulse times ranged from 0.5s to 2s. We propose a model for banding where Al2O3 nuclei grow in each cycle, thus the number of TMA adsorption sites increases. Due to the confined geometry, Knudsen diffusion and adsorption site density determine the relationship between precursor penetration depth and exposure time. The penetration depth is inversely proportional to the square root of the precursor adsorption site density and proportional to the square root of the exposure time. We have measured the penetration depth for different bands and a good fit to our model is shown.

3:20pm **TF+MI+NS-ThA4 NiOx Decorated Platinum Nanoparticles Via Atomic Layer Deposition for Enhanced Sintering Resistance**, ***Jiaming Cai***, *K. Cao, M. Gong, B. Shan, R. Chen*, Huazhong University of Science and Technology, PR China

Platinum nanoparticles (NPs) play an important role in the catalytic applications such as conversion of automotive exhaust, fuel cells, nano sensing and so on. For most catalytic applications, sintering of Pt NPs is undesired since the coalescence decreases the number of active sites of the catalyst. Herein we report the utilization of active oxide layers to encapsulate Pt NPs to enhance sintering resistance at high working temperature. The active oxide coated catalysts have additional metal-oxide interfaces which may further improve the catalytic activity besides good sintering resistance. Nickel oxide coating layer is prepared via atomic layer deposition (ALD) method. The effect of layer thickness towards catalytic properties and thermal stability for CO oxidation are investigated. The thickness of nickel oxide coating layer was controlled accurately by varying the ALD cycles. Characterizations including TEM, XPS, FTIR and XAFS were undertaken to explore the origin of the CO oxidation catalytic activity enhancement. *In-situ* AFM test is carried out to explore the mechanism of nanoparticles migration and sintering phenomenon in different environment by controlling the calcination temperature and oxygen partial pressure. Nickel oxide anchors Pt NPs with a strong metal oxide interaction, and coating structure around Pt NPs provide physical blocking that suppresses NP particle migration and coalescence. The catalysts show both enhanced CO conversion activity and improved sintering resistance up to 700 °C under oxidative atmospheric conditions.

4:00pm **TF+MI+NS-ThA6 Atomic Layer Deposition of HfO_2/Al_2O_3 Nanolaminates on Single-crystal GaN and Ga_2O_3: Investigation of Device Degradation in Power Semiconductor Devices**, ***David Mandia***, *A. Yanguas-Gil, J.A. Libera, J.W. Elam,* Argonne National Laboratory

The search for adequate binary metal oxide dielectric nanolaminates (NLs) to prevent degradation of power semiconductor devices is ongoing and involves the atomic layer deposition (ALD)-growth of a variety of binary metal oxide combinations. In the present work, we explore the ALD growth of amorphous $(x)HfO_2/(y)Al_2O_3$ NLs on Si (with native SiO_2 layer) substrates and then on both GaN and Ga_2O_3 single crystals. A variety of samples ranging from their homogeneous mixtures to HfO_2 or Al_2O_3-rich NLs are assessed before and after a thermal annealing by spectroscopic ellipsometry (SE), X-ray reflectometry (XRR), X-ray photoelectron spectroscopy (XPS) and 4-point probe resistivity measurements in order to elucidate the structural evolution of the NL at the GaN (or Ga_2O_3)-NL interface. By quantifying the HfO_2 incorporation throughout the Al_2O_3 layer and using the programmable nature of ALD to alternate layers of the HfO_2 and Al_2O_3 in an $(AB)_x$-$(CD)_y$ fashion, the influence of HfO_2 mobility within Al_2O_3 layer on the NL dielectric constant can be verified unequivocally. Moreover, combined X-ray absorption near-edge (XANES) and X-ray absorption fine structure (XAFS) spectroscopy data obtained at the Advanced Photon Source will confirm the local coordination environment of the Ga at the GaN (or Ga_2O_3)-HfO_2 interface and, at low super-cycle numbers (sub-nm scale), the ultimate stability of the NLs can be probed and optimized such that the bulk material properties are retained.

4:20pm **TF+MI+NS-ThA7 Atomic Layer Deposition Enabled Synthesis of Multiferroic Composite Nanostructures**, ***Jeffrey Chang****, University of California at Los Angeles, *A. Rosenberg*, Stanford University, *A. Buditama*, University of California at Los Angeles, *E. Jin, L. Kornblum, C. Ahn,* Yale University, *S.H. Tolbert,* University of California at Los Angeles, *K.A. Moler,* Stanford University, *J.P. Chang*, University of California at Los Angeles

Multiferroic materials, which 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 responses of single-phase multiferroics, composite strategies were proposed for a robust multiferroic behavior by coupling the functional properties through the interface. By interfacing magnetostrictive and piezoelectric materials, the strain-mediated coupling strategy holds great promise, while both the interfacial-area-per-volume and the quality of interfaces play important roles in attainable functional properties. To obtain applicable magnetoelectric (ME) coupling under such scheme, lead-free multiferroic $BiFeO_3$ (BFO) and ferrimagnetic $CoFe_2O_4$ (CFO) were used in this study due to their robust functionality.

With the aim of enhancing the coupling by nanostructuring, atomic layer deposition (ALD), with its high quality and conformal film growth, was

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*** TFD James Harper Award Finalist**

employed to achieve BFO/CFO composites with closely coupled interfaces and industrial scalability. BFO and CFO with were synthesized by radical enhanced ALD on SrTiO$_3$ (001) substrates using tmhd-based organometallic precursors(tmhd=2,2,6,6-tetramethylheptane-3,5 dione). The use of oxygen radicals as the oxidant provides a low temperature processing capability at 200°C. Post-deposition thermal treatments promotes the crystallization of both the BFO and CFO films and thus comparable functional properties were obtained. 2D-2D BFO/CFO composites were then synthesized by combining the ALD processes, with an optimized functionality obtained by nanolayering. ME behaviors comparable to previously studied multiferroic composites were observed, and the scaling of materials leads to an enhancement in the coupling coefficient (≈64 Oe cm/kV). The change in magnetic domains upon electrical poling was characterized using scanning SQUID. The 2D-2D BFO/CFO on SrTiO$_3$-buffered Si substrates exhibited comparable ME behaviors to the case on SrTiO$_3$, illustrating a path to integrate multiferroic materials into current industrial processes by ALD.

0D-3D BFO/CFO was realized by incorporating ALD-grown BiFeO$_3$ and mesoporous CFO substrates. Composite functionality as well as ME coupling were studied as a function of residual porosity after ALD filling. Higher BFO incorporation increases the overall ferroelectricity but limits the strain interaction due to a decreased mechanical flexibility. The strain interaction was verified by the change in lattice parameters observed using high-resolution XRD measurements. The results showed that the residual porosity is the key for ME coupling in a strain-mediated scheme.

4:40pm **TF+MI+NS-ThA8 Recent Developments in the Analysis of ALD/CVD Thin Film Conformality**, ***Riikka Puurunen***, Aalto University, School of Chemical Engineering, Finland **INVITED**

The downscaling of future semiconductor devices with increasing 3D character has lead to increasing demand of highly conformal thin films. Atomic layer deposition (ALD), based on the use of repeated, self-terminating reactions of typically at least two compatible reactants on a solid substrate, is often the only technique that can meet the conformality specifications. Conformal films made by ALD are also needed in other fields with intrinsic three-dimensionality requirements such as microelectromechanical systems (MEMS) and porous particle based applications (e.g., catalysis).

This work overviews recent progress in thin film conformality analysis made with the microscopic lateral high-aspect-ratio (LHAR), especially the “PillarHall” structures developed at VTT. Significant progress has taken place during the past year in the design and fabrication of the structures, conformality testing by academic and industrial partners, as well as modelling. The key feature of VTT’s PillarHall structures is the existence in silicon of a lateral gap of controlled height, typically 500 nm (can be varied from wafer to wafer, 100 to 2000 nm demonstrated), and controlled length up to 5 mm (several variations inside one chip, starting from 1 µm). Test structures with aspect ratio (AR) up to 50 000 : 1 ("hole-equivalent AR (EAR)" up to 25 000 : 1) have been fabricated this way. Growth of thin film inside the controlled 3-D gap and analysis of the film thereafter, often after removing the top part of the test structure by applying an adhesive, reveals the film thickness and composition profile. As compared to conventional vertical trenches etched into silicon, with VTT’s lateral PillarHall test structures, one can in a significantly shorter time obtain more detailed information on the conformality, which can be used for optimising processes, designing new processes, and investigating the fundamental mechanisms behind the deposition processes. Three scientific publications [1-3] report on the use of PillarHall 1st generation prototypes. At the time of writing this abstract, we work with 3rd generation prototypes and design the 4th generation.

Acknowledgements: Funding for the development of the conformality test structures has come from the Academy of Finland’s Finnish Centre of Excellence in Atomic Layer Deposition and the Tekes PillarHall project.

[1] Gao et al., J. Vac. Sci. Technol. A, 33 (2015) 010601 (5 pages). http://dx.doi.org/10.1116/1.4903941

[2] Mattinen et al., Langmuir 32 (2016) 10559-10569. http://dx.doi.org/10.1021/acs.langmuir.6b03007

[3] Puurunen & Gao, IEEE Xplore 2017, http://ieeexplore.ieee.org/document/7886526/

5:20pm **TF+MI+NS-ThA10 Spatial Atomic Layer Deposition Reactor Design for Nano-laminates**, *X.L. Wang*, ***Yun Li***, *J.L. Lin, J.M. Cai, R. Chen*, Huazhong University of Science and Technology, PR China

Atomic layer deposition (ALD) is commonly a vacuum based technique for ultrathin film fabrication with precise control of film thickness, uniformity and conformity. In contrast to conventional temporal ALD (T-ALD) that precursors and purging gases are introduced into reactor sequentially, the separation mode of spatially-separately ALD (S-ALD) between reactive precursors is in space instead of in time, thus the process is continuous. In S-ALD process, the inert gas serves as a flow gas barrier to separate the precursors’ zones, which prevents the cross contamination and atmosphere perturbation. With the alternating arrangements of oxidizer gas channels, metal source channels, and gas barriers of inert gas, the deposition rate of S-ALD could reach 1-3 order of magnitude higher than T-ALD. Moreover, the atmospheric pressure in S-ALD system enables this technique in a continuous form without vacuum. As the continuing development of S-ALD, it has found many potential high through-put and large scale applications. Here we present an S-ALD system design for fabricating binary oxides and their nano-laminates. The design of S-ALD reactor is based on motion structure of linear track and injector with a multiple slit gas source channel. By optimizing the structure of precursor channel based on the flow field simulation, a tree-branch-like gas feed structure is obtained, and the uniformity of the precursor distribution is enhanced significantly. The T-curve motion profile is replaced by the S-curve t o control the movement of substrate which can avoid abrupt change of acceleration and jerk in the acceleration and deceleration process, stabilizing the distance between injector and substrate precisely. The growth of thin film at different moving speeds has good linearity and uniformity. By integrating different reaction units, nano-laminates with tunable optical and electrical properties can be obtained.

Thin Films Division
Room: 20 - Session TF+MI-ThA

Control, Characterization, and Modeling of Thin Films II

Moderators: Subhadra Gupta, University of Alabama, Angel Yanguas, Argonne National Laboratory

2:20pm **TF+MI-ThA1 *In Situ* Monitoring of the Growth of Metallic, Nitride and Oxide Thin Films Prepared by Pulsed Laser Deposition**, ***Michal Novotny***, *J. Bulir, E. Maresova,* Institute of Physics ASCR, Czech Republic, *P. Fitl, J. Vlcek,* University of Chemistry and Technology Prague, Czech Republic, *M. Vondracek, L. Fekete, J. Lancok,* Institute of Physics ASCR, Czech Republic, *N. Abdellaoui, A. Pereira,* University of Lyon, Université Claude Bernard Lyon, France

Pulsed laser deposition (PLD) is a well-established technique in fabrication of thin films. PLD profits from its simplicity, modesty, versatility and flexibility. Varying deposition conditions, ie. fluence, laser repetition rate, ambient pressure, substrate and its temperature, one can easily influence nucleation and the growth of thin film and consequently its properties. The in-situ monitoring of electrical properties allows sophistically control such processes. We demonstrated the in-situ monitoring possibilities for aluminium and silver as metallic materials examples, titanium nitride and zirconium nitride as nitride materials examples, and zinc oxide and tin oxide as oxide materials examples. The films attract attention in eg. photonics, plasmonics, electronics, sensors and biophysics. Particular application requires the film of special morphology, ie. isolated nanoparticles, arrays, or smooth surface.

The targets of Al, Ag, TiN, ZrN, ZnO and SnO$_2$ were ablated by a Nd:YAG laser operating at wavelength of 266 nm and pulse length of 4 ns. The laser repetition rate was varied from 0.1 Hz to 10 Hz. Electrical conductivity and I-V curve were measured by four-wire technique.

The results of the in-situ monitoring are correlated with the AFM and SEM analyses of the surface morphology, optical properties characterized by spectral ellipsometry and composition studied by XPS. We are able to distinguish the growth mode in the real-time, estimate the point of coalescence as well as the subsequent evolution of the surface roughness and control it. The obtained results provide knowledge toward synthesis of novel functional materials for optoelectronics and sensors.

2:40pm **TF+MI-ThA2 Perpendicular Magnetic Anisotropy in CoxPd100-x Alloys for Perpendicular Magnetic Tunnel Junctions and Bit Patterned Media**, ***Subhadra Gupta***, *B.D. Clark, A.G. Owen*, University of Alabama

Materials with high Perpendicular Magnetic Anisotropy (PMA) have drawn intensive research interest in recent years. This is because they have applications in perpendicular magnetic tunnel junctions (p-MTJ) and perpendicular magnetic recording media. Often solutions to these problems require overly complicated multilayer structure or high temperature grown L1$_0$ alloy. We demonstrate a simple room temperature grown CoPd alloy that is characterized by Alternating Gradient Magnetometry (AGM), Energy-Dispersive X-ray Spectroscopy (EDS), and X-ray Diffraction (XRD). We have found that the PMA and coercivity is tunable based off thickness, composition, annealing, and seed layer. Current in-plane tunneling (CIPT) measurements were performed on the stack Si/ SiO$_2$ / MgO (13)/ CoxPd100-

x (50) / Ta (0.3) / CoFeB (1) / MgO (1.6) / CoFeB (1) / Ta (5) / Ru (10), with the numbers in parenthesis being the layer thickness in nm. CIPT data shows the highest magnetoresistance measurements correlates with the samples with the highest PMA. The stack Si / SiO_2 / Ta (5) / Pd (5) / $Co_{25}Pd_{75}$ (20) / Ta (5), with the numbers in parenthesis being the layer thickness in nm, were patterned using block copolymer templating and show an increase in coercivity from 3.3 kOe to 3.6 kOe with a nanopillar diameter approaching 10 nm, indicating that it may be suitable for bit pattern media (BPM) development.

3:00pm **TF+MI-ThA3 Combining Dynamic Shadowing Growth and Colloidal Monolayer to Design Plasmonic Metamaterials**, ***Yiping Zhao***, University of Georgia **INVITED**

The past decade has witnessed a rapid development of plasmonic metamaterials, which have unique optical properties and promising applications. Here, we report a simple, versatile, and scalable method for plasmonic metamaterial fabrication, which combines dynamic shadowing growth and self-assembled nanosphere monolayers, referred to as nanosphere shadowing lithography. In this method, a physical vapor deposition creates regular nanostructure arrays on modified nanosphere monolayers due to shadowing effect. The nanostructure morphology can be controlled by tuning the vapor flux direction with respect to the monolayers. Benefited from its control in nanostructure morphology, we have designed and fabricated a series of plasmonic nanostructures, including discrete nanoparticle arrays, nanoholes, nanoparticle networks, graded nanostructures, and chiral metamaterials such as patchy particles, helically stacked plasmonic layers, and Swiss roll structures. These well designed plasmonic nanostructures show tunable localized plasmonic resonance property and large circular dichroism response. In addition, by combining a co-deposition growth method, alloy or mixed phase plasmonic structures can be designed and investigated systematically. Such a simple but scalable fabrication method has a great potential for plasmonic metamaterial and meta-device development.

4:00pm **TF+MI-ThA6 Physical Vapor Deposition of Emerging Resistive Memories**, *M. Pakala*, ***Lin Xue***, Applied Materials, Inc. **INVITED**

We are getting deeper into the memory centric computing era, with emerging non-volatile memories being rapidly developed to fill gaps in latency, density and functionality. Various types of resistive memories such as STT MRAM, ReRAM and PCRAM are being developed to augment characteristics of available charge based memories. This is driving new deposition process / equipment requirements for these materials, since many of these materials are non-standard materials for an existing semiconductor fab. In my presentation, I will cover the requirements for depositing such materials as well as factors that drive these requirements. Particular focus will be on depositing magnetic tunnel junction stacks for STT MRAM as well as other semiconductor/oxide materials for resistive memories and selectors that can enable high density cross point memory.

4:40pm **TF+MI-ThA8 Metal Oxide Nanostructure Growth by a Simple Hot Water Deposition (HWD) Method**, ***Nawzat Saadi***, *T. Karabacak*, University of Arkansas at Little Rock

We are presenting a new hot water deposition (HWD) method to grow metal oxide nanostructures (MONSTRs). The technique is simple, low cost, low temperature, scalable, high-throughput, and does not involve any chemical agents or surface activators. Moreover, HWD can be used to deposit a large variety MONSTR materials on almost any type of substrate material or geometry. The process simply involves a source metal and a target substrate that are both immersed into hot water. The water temperature during HWD is typically between 50-95 ºC. In this work, we demonstrate that zinc oxide (ZnO) MONSTRs can be deposited on different substrates including copper (Cu) plate, Cu mesh, Cu foam, and ITO coated glass. We used Zn plate and powder as the source. Temperature of the water was set to 75 ºC. We observed that ZnO nanowires with lengths of few hundreds of nanometers and hexagonal cross-sections of about 50-100 nm grew within about 3 hours. ZnO MONSTRs covered the target substrates uniformly including the 3D foam surface. Smooth facets observed in SEM images and XRD results indicate that ZnO nanostructures have a well-developed crystal structure. In addition, we present a growth mechanism that includes the main processes of "plugging" and surface diffusion. The plugging involves the steps of metal oxide formation on metal-source surface, release of metal oxide molecules from the source, migration trough water, and deposition on the target surface. This is followed by surface diffusion of metal oxide molecules that help forming MONSTRs with smooth crystal facets. We also claim that "shadowing" effect can play an important role and promotes MONSTR growth on taller hills of the target surface vs valleys. We performed experiments such as HWD at different substrate-target distances, target roughness, and deposition time in order to better understand the contribution of each step listed above.

5:00pm **TF+MI-ThA9 Microsphere-Based Disordered Coatings for Effective Radiative Cooling**, ***Sarun Atiganyanun***, *J. Plumley, K. Hsu*, University of New Mexico, *J. Cytrynbaum*, Williams College, *T. Peng*, Air Force Research Laboratory, *S.M. Han, S.E. Han*, University of New Mexico

Being able to cool the buildings below the ambient temperature under the sun in the middle of a summer without having to use air conditioning would result in tremendous energy savings. As a step towards this goal, we have investigated a facile application of coatings made of silica microspheres in disordered structures, using evaporation as well as spray-coating. For the evaporation coating, silica microspheres are dispersed in water, and the colloidal stability is disrupted by dissolving ionic salt into the solution. The colloidal solution is confined onto a substrate and is allowed to evaporate. For the spray-coating, much like commercial painting, the aqueous colloidal solution is forced through a spray nozzle and deposited onto a substrate. Scanning electron microscopy images and autocorrelation analyses 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 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 estimate the theoretical limit, a computational model is first used to calculate the cooling power of the coatings under direct sunlight. The model predicts that the disordered coating with 200 μm thickness has a cooling power of ~250 W/m^2 at 27ºC and could reduce the temperature of the sample under the direct sunlight by approximately 37ºC below the ambient temperature. Our experimental measurements under direct sunlight show that our coatings perform better than commercial sunlight and heat reflective paints. We will further discuss how coatings of disordered, random, inverse structures can enhance the durability of our coating in a paint format, while maintaining radiative cooling properties.

5:20pm **TF+MI-ThA10 Sputter Beam Epitaxy: Innovation towards Spin Control in Intermetallic Thin Films**, ***Adam Hauser***, The University of Alabama **INVITED**

The vast array of interesting crystal structures and the wealth of elemental choices guarantee that we are never lacking for new opportunities in designing and making "custom-built" materials, if a method can be devised to build these complex materials systems. This talk will highlight our progress in thin film growth via Sputter Beam Epitaxy, an approach combining the fabrication strengths of off-axis magnetron sputtering and molecular beam epitaxy. We will focus on highly-ordered B2 alloys (including the Heusler sub-class) with an eye towards determination of the true properties of ideally ordered materials and tuning towards ideal spin damping properties.

2D Materials Focus Topic
Room: 15 - Session 2D+MI+NS+SS+TF-FrM

Nanostructures including Heterostructures and Patterning of 2D Materials

Moderators: Huamin Li, University of Buffalo, SUNY, Arkady Krasheninnikov, Helmholtz Zentrum Dresden-Rossendorf, Germany

8:20am **2D+MI+NS+SS+TF-FrM1 Electro-optics with 2D Semiconductors and Heterostructures**, ***Goki Eda***, National University of Singapore, Singapore **INVITED**

Despite being only a few atoms thick, two-dimensional (2D) semiconductors such as monolayer MoS_2 and phosphorene exhibit distinctly strong light-matter interaction compared to their bulk counterparts. Excitons and their complexes with giant oscillator strength play a fundamental role in mediating the strong coupling between light and a 2D semiconductor. These excitons are stable at room temperature and make 2D semiconductors attractive for a number of photonic devices including ultra-fast photo-detectors, optical modulators, on-chip photonic circuits, flexible photovoltaic devices, chiral light emitters, single photon sources, and ultra-low threshold lasers[1]. In order for these devices to be integrated for photonic devices, practical schemes for electrical generation, manipulation, and detection of excitons need to be developed. We create artificial quantum wells based on van der Waal heterostructures and investigate the dynamics of 2D excitons under various conditions to achieve the desired photonic functionalities. In this talk, I will start by discussing our findings on the ultrafast dipole-dipole energy transfer processes involving 2D excitons. I will show that exciton-exciton energy transfer in hetero-bilayers is among the fastest measured in nanomaterials[2]. Peculiar optical effects arising from strong exciton-plasmon coupling in 2D semiconductors hybridized with metal nanoparticles will also be discussed[3]. Finally, our recent efforts in realizing electro-optical (electroluminescence, electro-absorption, and Pockels effect) devices will be discussed. I will share our views on the potential advantages of 2D semiconductors over other materials and discuss our outlook for further studies.

References:

1. F. Xia et al. “Two-dimensional material nanophotonics” Nat. Phot. 8, 899 (2016).

2. D. Kozawa *et al*. "Efficient interlayer energy transfer via 2D dipole coupling in $MoSe_2/WS_2$ heterostructures" Nano Lett. 16, 4087 (2016).

3. W. Zhao *et. al*. “Exciton-plasmon coupling and electromagnetically induced transparency in monolayer semiconductors hybridized with Ag nanoparticles” *Adv. Mater.* 28, 2709 (2016).

9:00am **2D+MI+NS+SS+TF-FrM3 Understanding Variations in Circularly Polarized Photoluminescence in Monolayer Transition Metal Dichalcogenides**, ***Kathleen McCreary***, *M. Currie, A.T. Hanbicki, B.T. Jonker*, Naval Research Laboratory

The unique electronic band structure in monolayer transition metal dichalcogenides (TMDs) provides the ability to selectively populate a desired conduction band valley by exciting with circularly polarized light. The subsequent valley population can be interrogated by measuring helicity-resolved photoluminescence (PL). A high degree of circular polarization has been theoretically predicted for resonant excitation of TMDs, yet rarely observed experimentally. In fact, a wide range of values for the degree of circularly polarized emission (P_{circ}), has been reported for monolayer TMDs, although the reasons for the disparity are unclear. Here we investigate the room-temperature P_{circ} in several TMD monolayers synthesized via chemical vapor deposition. The samples include as-grown WS_2, as-grown WSe_2, and WS_2 monolayers that have been transferred to a fresh substrate. In each system, a wide range of P_{circ} and PL intensity values are observed. There is a pronounced inverse correlation between P_{circ} and PL intensity: samples that demonstrate weak PL emission and short exciton relaxation time exhibit a high degree of valley polarization. We attribute these effects to sample-dependent variations in the exciton radiative and non-radiative lifetime components. The short exciton lifetime results in a higher measured polarization by limiting opportunity for depolarizing scattering events. These findings clarify the disparities among previously reported values and suggest a means to engineer valley polarization via controlled introduction of defects and non-radiative recombination sites.

This work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #AOARD 14IOA018-134141.

9:20am **2D+MI+NS+SS+TF-FrM4 Multi-Junction Lateral 2D Heterostructures of Transition Metal Dichalcogenides**, ***Prasana Sahoo***, University of South Florida, *S. Memaran*, Florida State University, *Y. Xin*, National High Magnetic Field Laboratory, *L. Balicas*, Florida State University, *H.R. Gutierrez*, University of South Florida

Here we demonstrate the successful synthesis of lateral in-plane multi-junction heterostructures based on transition metal dichalcogenides (TMD) 2D monolayers. The heterostructures were synthesized using a modified chemical vapor deposition approach. By only controlling the carrier gas composition, it is possible to selectively growth only one TMD at the time. This introduces an unprecedented flexibility in the CVD process and allows a good control of the lateral size of each TMD segment. Heterostructures only containing MoS_2-WS_2 or $MoSe_2$-WSe_2 multiple segments, were fabricated. We also demonstrate the synthesis of heterostructures based on homogeneous TMD ternary alloys (MoS_xSe_y-WS_xSe_y). Introducing ternary alloys in heterostructures opens the horizon of possible chemical combinations and applications of 2D optoelectronic devices. The band gap modulation as well as spatial chemical distribution were studied by Raman and photoluminescence mapping. The crystalline quality of the heterostructures were characterized within an aberration-corrected scanning transmission electron microscope. Basic devices were also fabricated to study the transport properties across the junctions. Depending of the growing conditions, diffuse and/or sharp seamless interfaces with high-crystalline quality can be produced.

9:40am **2D+MI+NS+SS+TF-FrM5 Novel Electronic, Optoelectronic, and Topological Properties of 2D Materials and Their Heterostructures**, ***Xiaofeng Qian***, Texas A&M University **INVITED**

Low-dimensional materials exhibits dramatically distinct properties compared to their 3D bulk counterpart. 2D materials is such a fascinating platform with many exotic physical properties and unprecedented opportunities. In this talk, I will highlight some examples of interesting 2D materials and their heterostructures, including 2D multiferroics, 2D topological insulators and topological crystalline insulators, 2D nanostructured exciton funnels. First, I will present our discovery of 2D multiferroics in semiconducting Group IV monochalcogenide monolayers with giant spontaneous in-plane ferroelectric polarization and ferroelastic lattice strain that are strongly coupled. The multiferroicity and hence anisotropic 2D excitonic responses as well as low domain wall energy and migration barrier suggest their great potentials for tunable multiferroic functional devices such as 2D ferroelectric and ferroelastic memory, 2D ferroelastoelectric nonvolatile photonic memory, and 2D ferroelectric excitonic photovoltaics. In the second example, I will highlight our discovery on 2D topological insulators in binary and ternary transition metal dichalcogenides, and topological crystalline insulators in monolayer IV–VI semiconductors. We found electric field, elastic strain, and van der Waals stacking are able to induce topological phase transition (TPT), among which the electric-field induced TPT can be utilized for realizing topological field effect transistor distinctly different from conventional MOSFET. In the third example, I will discuss how macroscopic responses of materials can be tuned and configured by nanostructuring such as inhomogeneous strain engineering and van der Waals Moire patterning. Both nanostructures can modify local atomistic configurations and generate spatially varying electronic structures, thereby introducing novel excitonic photon funneling effect. The latter could be exploited for developing more efficient photovoltaics and light-emitting diodes. Finally, I will highlight relevant experimental progresses as well as some critical challenges and opportunities in 2D materials and their nanostructures.

10:20am **2D+MI+NS+SS+TF-FrM7 Imaging Nanoscale Heterogeneity at the Two-dimensional Semiconductor-Metal Heterointerface by Correlated Scanning Probe Microscopy**, ***Deep Jariwala****, California Institute of Technology, *A. Krayev, E. Robinson*, AIST-NT Inc., *M.C. Sherrott*, California Institute of Technology, *M. Terrones*, Pennsylvania State University, *H.A. Atwater*, California Institute of Technology

Transition metal dichalcogenides (TMDCs) of molybdenum and tungsten have recently attracted significant attention due to their band gaps in visible part of the spectrum for optoelectronic device applications. The ability to isolate these materials down to a monolayer with direct band-gap make TMDCs very attractive alternatives to graphene.

*** NSTD Postdoc Finalist**

While a lot of investigation has been devoted to understanding of crystalline and electronic quality of TMDCs in devices, little is known about the spatial distribution of electronic quality and interfaces with metals. Conventional Raman spectroscopy and confocal Raman microscopy have proved to be useful tools in this regard. However, the spatial resolution of these techniques is diffraction limited to a few hundred nanometers only. Tip enhanced Raman scattering (TERS) provides spatial resolution down to few nanometers, along with increased sensitivity due to dramatic enhancement of the Raman signal by the plasmonic tip and is therefore a suitable technique to probe nanoscale heterogeneity in TMDC samples.

Here, we report observation of nanoscale heterogeneity in exfoliated WSe$_2$ flakes on plasmonic Au and Ag substrates using a combination of spatial mapping with TERS, contact potential difference, topography and conductance measurements. In TERS mapping of exfoliated WSe$_2$ flakes, we observe the presence of domains with enhanced or depreciated Raman signal compared to adjacent material. We also observe that WSe$_2$ demonstrates a resonant Raman response with 638nm excitation, the TERS spectra of these domains feature a single peak at around 250 cm^{-1}, typical for non-resonant conditions. Distribution of these domains correlates extremely well with surface potential map, non-resonant areas being negatively charged compared to adjacent areas of WSe$_2$ that demonstrate a resonant Raman response.

We further correlate the TERS maps with concurrently recorded photocurrent maps, where we observe that domains showing both resonant and non-resonant Raman response, generated significant photocurrent, but of opposite polarities. Based on this observation, we conclude that in exfoliated layers of WSe$_2$, there exist nanoscale semiconducting domains with opposite doping types when in contact with the underlying metal. This hitherto unobserved heterogeneity is therefore critical to understanding of the metal-two dimensional (2D) semiconductor contact and important for optoelectronic device design and performance. The results presented here show that cross-correlation of TERS with local conductivity, surface potential and photocurrent is a vital characterization technique for nanoscale in-homogenities in 2D semiconductors and devices.

10:40am **2D+MI+NS+SS+TF-FrM8 Two-dimensional Circuitry Achieved by Defect Engineering of Transition Metal Dichalcogenides**, ***Michael G. Stanford****, *P.R. Pudasaini, A.N. Hoffman, P.D. Rack*, The University of Tennessee Knoxville

Two-dimensional materials, such as transition metal dichalcogenides (TMDs), have demonstrated promising semiconducting properties. The electrical and optical properties of TMDs can be fined tuned by altering material thickness as well as chemical composition. Properties can also be tuned by defect engineering. In this work, a focused He$^+$ beam as well as a remote plasma source were utilized to introduce defects into TMDs such as WSe$_2$ and WS$_2$ with fine control. Scanning transmission electron microscopy reveals that defects introduced into the TMDs range from chalcogen vacancies (0D defects) to 1D defects and extended defect networks. Tailoring defect concentration enables tunability of the electronic properties with insulating, semiconducting, and metallic behavior each obtainable. By tuning electronic properties, we demonstrate direct-write logic gates such as resistor loaded inverters with a voltage gain of greater than 5. We also demonstrate the fabrication of edge-contacted field effect transistors by defect engineering homojunctions between metallic and semiconducting WSe$_2$ with on/off ratios greater than 10^6. Defect engineering of TMDs enables the direct-write of complex devices into single flakes toward the goal of atomically thin circuitry.

11:00am **2D+MI+NS+SS+TF-FrM9 Scanning Tunneling Microscopy and Spectroscopy Studies of Atomically Precise Graphene Nanoribbons on Semiconducting Surfaces**, ***Ximeng Liu***, *A. Radocea, T. Sun,* Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, *M. Pour,* Nebraska Center for Materials and Nanoscience, University of Nebraska - Lincoln, *N. Aluru,* Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, *A. Sinitskii,* Nebraska Center for Materials and Nanoscience, University of Nebraska - Lincoln, *J.W. Lyding*, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign

Graphene nanoribbons (GNRs) with atomically smooth edges, controllable geometry and therefore tunable electronic band gaps have ignited enormous interest due to their high potential for future electronic devices. Among different techniques for GNR characterization, scanning tunneling microscopy and spectroscopy (STM/STS) provide both topographic details and local electronic structure with atomic resolution. Large-scale production of two different kinds of chevron-type GNRs (the double-wide (w) GNRs and the extended chevron (e) GNRs) was realized by a solution synthesis method [1]. Dry contact transfer technique [2] was implemented for depositing the solution-synthesized GNRs onto clean InAs (110) and hydrogen-passivated Si(100) semiconducting surfaces under ultrahigh vacuum conditions. For both GNRs, their structures were confirmed by high resolution STM imaging. The band gap of the eGNRs was determined to be 2.6eV via STS. For the wGNRs, detailed analysis and mapping of the electronic density of states both spatially and energetically was carried out with STS and current imaging tunneling spectroscopy. We found that the electron orbital shapes at the GNR edges are different from those at the centers, in agreement with computational simulations. The measured band gap of the wGNRs was only 2eV, which may result in a great improvement in conductivity. In addition, these GNRs are found to be transparent to the substrate when scanned at a small tip-sample separation, indicating a strong interaction when GNRs are pushed towards the substrate.

References:

1. Vo, T. H.; Shekhirev, M.; Kunkel, D. A.; Morton, M. D.; Berglund, E.; Kong, L. M.; Wilson, P. M.; Dowben, P. A.; Enders, A.; Sinitskii, A., Large-Scale Solution Synthesis of Narrow Graphene Nanoribbons. *Nat. Commun.* **2014,***5*, 3189.

2. Ritter, K. A.; Lyding, J. W. The influence of edge structure on the electronic properties of graphene quantum dots and nanoribbons. Nat. Mater. 2009, 8 (3), 235−42.

11:20am **2D+MI+NS+SS+TF-FrM10 Perfectly Perforated Monolayer WSe$_2$**, ***Kirby Smithe***, *C. Bailey,* Stanford University, *A. Krayev,* AIST-NT Inc., *E. Pop,* Stanford University

One of many prospective applications of 2D transition metal dichalcogenides (TMDs) is catalytic splitting of water for hydrogen generation. Strain in TMD layers, chalcogen atom vacancies, and increased length of the edges of TMD flakes all play an important role in increased catalytic activity, with the latter being the most effective way for improving performance. One possible way to achieve increased ratios of edge length to surface area is to use small flakes, preferably a few hundred nm across. Unfortunately, such small flakes are difficult to manipulate, and the structure of such flakes should also differ from the perfect structure of the inner areas of larger flakes[1]. Here we report that WSe$_2$ monolayers, grown by chemical vapor deposition (CVD) on Si/SiO$_2$ and transferred from the original substrate by means of dissolving the sacrificial SiO$_2$ layer, contain a significant concentration of perfect triangular holes. The result is confirmed by correlating the data of topography, the surface potential, friction and tip enhanced Raman spectroscopy (TERS) characterization of transferred flakes. The ratio of edge length to surface area in such perforated flakes could be up to 3 to 4 times higher compared to homogenous continuous flakes. These perforated flakes can be transferred to any surface, including corrugated ones, which should inevitably cause some strain that is also beneficial for hydrogen catalytic activity. The perfect triangular shape of the holes suggests high quality of the atomic structure of the hole edges, which also implies that the perforated flakes can be used as templates for growth of distributed in-plane heterostructures of different TMDs.

1. Nature Commun., Wei Bao*, Nick Borys*, et al. “Visualizing nanoscale excitonic relaxation properties of disordered edges and grain boundaries in monolayer molybdenum disulfide,” 6, 7993 (2015)

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* **National Student Award Finalist**

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