## Biomaterials Plenary Session
## Room: 22 - Session BP-SuA

### Plenary - Engineering a Paradigm Shift in Control of Microbes and Fouling: In Honor of Michael Grunze's 70th Birthday
**Moderator:** Axel Rosenhahn, Ruhr-University Bochum, Germany

3:00pm **BP-SuA1 Non-toxic Surfaces which Prevent Biofouling:Quo Vadis?**, ***Michael Grunze***, Karlsruhe Institute of Technology (KIT), Germany **INVITED**

Biofouling, i.e. the settlement and colonization of bacteria and spores on surfaces is a major economic and environmental problem. Besides the obvious problems which biofouling causes in the clinical environment, biofouling is a serious problem also in food processing, aquacultures, shipping, underwater structures and ship hulls, heat exchangers, and buildings in tropical environments. The common—but environmentally extremely problematic—way to deal with biofouling is to incorporate heavy metals and/or biocides to kill the colonizing organisms. Hence, there is an urgent need to develop environmental benign stable and long lasting coatings to prevent biofouling.

The biofouling environment consists of multiple and often cooperatively interacting species of various sizes. Significant differences in the initial settlement behavior of bacteria, spores, larvae, and diatoms are observed on different chemical surface compositions, but the continuous deposition of dissolved macromolecules and polymers on “inert chemistries” leads to a “conditioning film” which soon renders any chemical modification of the surface ineffective. Topographic structures on surfaces change the macroscopic properties such as their wetting behavior, but also have a pronounced effect on how single cells and organisms attach, settle, and proliferate on the substrate. Both the enhancement of settlement, such as in cell cultures, but also the suppression of settlement can be the outcome of surface structuring. Promising are slippery liquid-infused porous surfaces (SLIPSs) which have been reported for their remarkable initial antifouling properties. However, their long-term stability against fouling is compromised by unavoidable defects in the SLIPS surface, and the slow deposition of a conditioning film.

In this presentation, I discuss if present research and development approaches are successful in creating lasting non-toxic non-fouling coatings for artificial surfaces. I will outline the different concepts to fouling prevention, and the challenges and technical difficulties encountered to realize long term stability and efficiency against fouling.

3:40pm **BP-SuA3 Engineering Serendipity: High-throughput Discovery of Materials that Resist Bacterial Attachment**, ***Morgan Alexander***, The University of Nottingham, UK **INVITED**

Tackling medical device centred infection is an important part of meeting the global challenge of antimicrobial resistance. We focus on materials that resist bacterial attachment and biofilm formation rather than kill the cells, since it is anticipated that the selective pressure to develop antimicrobial resistance will be lower. High throughput screening has been used to discover a novel class of polymers with resistance to bacterial attachment and subsequent biofilm formation. [Hook et al. Nat.Biotech. 2012, Adv.Mats. 2013] In order to rationally design devices for medical application and others where biofilm formation is a challenge, we are developing a fundamental understanding of the processes involved in the interaction of bacterial cells with our lead materials.

Physicochemical descriptions of the surfaces have been found insufficient to predict bacterial attachment across diverse chemistries included in large polymer libraries, and therefore cannot offer an explanation of the controlling phenomena. Whilst perhaps disappointing for the physical sciences, the life sciences are replete with information on how bacteria respond to their local environment, with motility being one of the most readily observed processes. Microorganisms cannot be approximated to inert objects as they possess surface responsive appendages such as flagella, which enable them to swim, pili that confer twitching motility and fimbriae that mediate surface attachment. These in turn are coupled to sophisticated signal transduction mechanisms that facilitate integration of multiple local environmental parameters at both single cell and population levels. Many of these sensory systems are postulated to contribute to surface sensing.

We believe that bacterial decision-making is key to determining whether a surface is colonised or not-specifically in the early stages of bacterial-surface interactions preceding biofilm formation. I will present results from our optical microscopy investigations of how individual bacterial cells respond to surfaces using a novel microscope that collects temporal 3D information on cell position and surface tracking simultaneously achieved using DIC, TIRF and TIR microscopy. I will combine this information with our early efforts to characterise bacterial footprints and compare with literature for *P. aeruginosa* where the exopolysaccharide Psl guides surface exploration [Zhao et al Nature 2013]. Elucidation of the sensory pathways by which bacteria decide not to form biofilms on some surfaces is expected to have wide ranging impact in all areas where biofilms form.

4:20pm **BP-SuA5 Say ‘No’ to Biofouling: Slippery Coatings that Resist Adhesion of Biological Matter**, ***Joanna Aizenberg***, Harvard University **INVITED**

Living organisms and biological substances are among the most difficult and persistent sources of surface fouling, particularly in medical and marine settings. The ability of organisms to adapt, move, cooperate, evolve on short timescales, and modify surfaces by secreting proteins and other molecules enables them to colonize even state-of-the-art antifouling coatings, and small surface defects can trigger protein aggregation and blood clotting. Attempts to combat these issues are further hindered by conflicting requirements at different size scales and across different species. Our recently developed concept of Slippery, Liquid-Infused Porous Surfaces (SLIPS) provides a defect-free, dynamic liquid interface that overcomes many of these problems at once. A single surface is able to prevent adhesion of a broad range of genetically diverse bacteria, including many pathogenic species that underlie widespread hospital-acquired infections, as well as marine algae. The same approach resists adhesion of proteins, cells, and blood, preventing clogging and thrombus formation inside medical tubing and catheters. At a larger scale, the slippery interface repels insects, barnacles and mussels, which slide off and actively avoid the coated surface. We are currently developing this strategy to solve longstanding fouling issues in a wide range of medical, marine, and other settings.

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## 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:

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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.

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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.

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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.

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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 $\mu_B/U^{3+}$ 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 $\mu_B/U^{3+}$. 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.

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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 $\gamma$, which reaches 440 mJ/mol f.u. $K^2$ ($\gamma$ = 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 $CeMIn_5$ ($M$ = 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.

[1] L. Yedra et al., Sci. Rep. 6, 28705, 2016

[2] T. Wirtz et al., Nanotechnology 26 (2015) 434001

[3] T. Wirtz et al., Helium Ion Microscopy, ed. G. Hlawacek, A. Gölzhäuser, Springer, 2017

[4] P. Gratia et al, J. Am. Chem. Soc. 138 (49) 15821–15824, 2016

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.

[1] Ninomiya, S ; Ichiki, K ; Yamada, H ; Nakata, Y ; Seki, T ; Aoki, T ; Matsuo, J Rapid Comm. Mass Spec. **23** 20 (2009) 3264.

[2] Miyayama, T ; Sanada, N ; Bryan, SR ; Hammond, JS ; Suzuki, M ; Surf. Interface Anal. **42** 9 (2010) 1453

### 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.

## Biomaterial Interfaces Division
## Room: 12 - Session BI-MoM

## Engineering a Paradigm Shift in Control of Microbes and Fouling
**Moderators:** Joe Baio, Oregon State University, Daniel Barlow, US Naval Research Laboratory

8:20am **BI-MoM1 Characterization of Adult Barnacle Adhesion Upon Reattachment to Hydrophobic Surfaces**, ***Manuel Figueroa***, *G. Dickinson*, The College of New Jersey

Although a wide range of environmentally friendly surface coatings can reduce biofouling on marine structures, there is still not a fundamental understanding of barnacle adhesion upon reattachment. This study assessed the effect of hydrophobicity on adhesion in the barnacle *Amphibalanus amphitrite*, an abundant and widespread biofouler. Self-assembled monolayers were made on glass slides from alkyl silanes with methylated and fluorinated terminal groups to produce hydrophobic surfaces. Coated and uncoated glass slides underwent a 2-week barnacle reattachment assay. Barnacles were removed using a force gauge and critical shear stress was calculated for each substrate. Following reattachment assays, a Coomassie Blue G250 protein stain was used to quantify the amount of glue remaining on substrates by measuring pixel density with ImageJ software on glue scans.

Critical shear stress was found to be significantly higher for both hydrophobic surfaces as compared to the hydrophilic uncoated glass, and correspondingly the density of residual glue was higher on hydrophobic surfaces. Given that hydrophobic substrates can exclude water from the surface, they may provide a protected environment for glue release that is favorable for adhesive bond formation with the substrate as well as inter and intramolecular bonding within the glue layer. Critical shear stress showed a strong positive correlation with residual glue density, suggesting barnacle release occurs primarily via cohesive failure. Scanning electron microscope micrographs depicted a diverse mixture of features in the glue remnants depending on the coating and its location under the base plate. These features, which included a sponge-like matrix, globular structures, viscous fingering and nanoscale fibers contribute to adhesion strength. The design of marine coatings must continue to consider the nanoscale topography as an essential attribute to reducing biofouling as well as the ability of a coating to exclude water from the surface.

8:40am **BI-MoM2 Constructing and Deconstructing the Barnacle Adhesive Interface**, *C.R. So, K.P. Fears*, US Naval Research Laboratory, *H. Ryou*, ASEE Research Fellow at US Naval Research Laboratory, *D.E. Barlow, D.H. Leary, J.A. Wollmershauser, C.M. Spillmann*, ***Kathryn Wahl***, US Naval Research Laboratory

Barnacles are sessile marine arthropods that live and reproduce on nearly any available surface in the ocean. They adhere via a thin adhesive layer developed through a multistep secretory process synchronized with growth via molting. Unlike other arthropods, the combination of expansion, molting and protein secretion within the narrow adhesion interface leads to a nanofibrillar protein layer manipulated by shear stresses, protected by calcite, and containing a cocktail of chemically active molecules and proteins. Here we use *in vivo* imaging, mechanics, and spectroscopy of barnacle growth and development, coupled with mass spectrometry and proteomics to reveal much about the biophysics and biochemistry of barnacle adhesion. We will discuss the role of interfacial processes, self-assembly, amino acid composition, and chemical manipulation in the construction and function of the adhesive.

9:00am **BI-MoM3 Live Confocal Microscopy of *Balanus Amphitrite* Reveals Anti-Fouling Strategy of a Marine Fouler**, ***Kenan Fears***, US Naval Research Laboratory, *B. Orihuela, D. Rittschof*, Duke University Marine Laboratory, *K.J. Wahl*, US Naval Research Laboratory

The adhesion of hard foulers (e.g., barnacles and tubeworms) has plagued the maritime community for as long as mankind has been setting sail. Since the biological processes responsible for adhesion occur at buried interfaces, elucidating the mechanisms by which foulers adhere is challenging. Through the use of multiple fluorescent probes, peptides, and antibodies, we have been able to discern an unprecedented level of detail about biological processes that occur at the interface between acorn barnacles (Balanus Amphitrite) and the underlying substratum during the barnacle growth cycle. Barnacles secrete a lipidaceous substance around the outside of their shell, prior to expansion that dislodges microorganisms and biofilms to present a cleaned surface. During molting, epithelia cells build a new interfacial cuticular layer, which becomes autofluorescent as it is sclerotized, above the existing cuticle whose degradation coincides with the exuviation of the main body's cuticle. Rather than being directly secreted onto the substrate, nanostructured barnacle cement accumulates in the space in between the new and old cuticle. As the barnacle expands, the cuticular layers are stretched and pulled around the outside of the side plate. The strain causes the old cuticle to randomly tear, allowing the new cuticle to deposit cement into the interface as it is dragged across the substrate. Furthermore, antibody staining allowed us to spatially and temporally identify where different cement proteins are presenet. These results illustrate that the methodologies we have developed to break down and analyze barnacle cement collection are yielding a more accurate representation of the proteins at the buried interface, and providing insight on their roles which will lead to improved strategies to both combat and mimic barnacle adhesives.

9:20am **BI-MoM4 Considering the Consequences of a Paradigm Shift in Biofouling Management**, ***Daniel Rittschof***, *B. Orihuela*, Duke University, *K. Efimenko, J. Genzer*, NC State University

Present Fouling Management Strategies that use long-lived, broad-spectrum biocides are not sustainable because they alter ecosystem services and threaten food security. As globalization continues, human populations increase and wild fisheries collapse there will be increasing pressure and genuine need for less environmentally damaging approaches. A question that should be asked up front for any new fouling management technology is what are the environmental, food security and human health consequences if a technology gains market share. Information on impacts of industrial grade components, acute and chronic toxicity, breakdown and non-toxic biological effects such as teratogenicity, carcinogenicity and environmental steroid activity should be evaluated. This presentation looks at a few of the details of basic silicone coatings which have had their components purified and then tested for acute toxicity, impacts on a hydrolytic enzyme and teratogenicity. Some components like catalysts and small cyclics are extremely toxic. Other components impact enzyme activity, some inhibit activity other potentiate activity. Terratogenicity assays are so sensitive that even effects of medical grade silicones can be demonstrated. This information needs to be taken as preliminary factual information that can be used by engineers in developing risk benefit analysis.

9:40am **BI-MoM5 Microbiological Fouling on Aircraft: Understanding the Mechanisms of Polyurethane Topcoat Deterioration by Fungal Isolates**, ***Daniel Barlow***, *J.C. Biffinger*, US Naval Research Laboratory, *C.-S. Hung*, Air Force Research Laboratory, *L.J. Nadeau*, Air Force Institute of Technology, *A.L. Crouch, T. Zicht*, Air Force Research Laboratory, *J.N. Russell, Jr.*, US Naval Research Laboratory, *W.J. Crookes-Goodson*, Air Force Research Laboratory

Fungal and bacterial fouling on military aircraft is a problem that can lead to polyurethane top coat deterioration and pose health hazards to personnel; the phasing out of hexavalent chromium in coatings is expected to worsen fouling problems. Thus, better understanding of the relevant microbiological interactions with polyurethanes is required to identify new ways to inhibit fouling and associated affects. We have screened over 400 aircraft isolates for polyurethane degradation, with Cryptococcus strains among the most aggressive polyurethane degraders. These strains were further characterized for their capability to metabolize and grow on expected hydrolysis products from polyester components of the polymers, showing that fungal growth occurs to varying degrees on the metabolites. Gas chromatography also showed that microbes metabolize polymers and hydrolysis products to $CO_2$. Polymer metabolization to $CO_2$ results in bulk polymer loss and optical profilometry confirmed that fungal cells steadily “eat” trenches into solid polyurethane films over time. Initial polyurethane film degradation processes at the micro and nano scales were analyzed by confocal Raman and AFM-IR (combined AFM and infrared spectroscopy). These results showed varying, non-uniform degradation events among cells, indicating that variations in single cell physiology play roles in early stage degradation. The spectroscopic results are consistent with lipase activity as the primary driver of degradation.

10:00am **BI-MoM6 Dynamic Accumulation Assays under Laminar Flow Conditions to Probe Attachment of Marine Biofilm Formers**, ***Kim Alexander Nolte***, *J. Schwarze, A. Rosenhahn*, Ruhr-University Bochum, Germany

Novel materials with environmentally benign fouling-release properties have been developed during the last years to substitute toxic coatings. Assessment of fouling-release coating's efficiency is of key relevance for the down selection of chemistries. Several techniques are accessible that quantify, how easy fouling organisms can be removed, including calibrated, turbulent flow channels, push-off tests, water jets, and microfluidic devices [1, 2]. We developed a laboratory assay based on a parallel plate flow chamber that allows testing of coating candidates against algal cell adhesion with precisely controlled flow rates and cell concentrations. Using self-assembled monolayers as model surfaces and diatoms as model organisms we were able to show that the adhesion strength [1] correlates with the accumulation dynamics if an appropriate wall shear stress is applied. Similar to the critical wall shear stress for removal assays, a range of wall shear stresses was identified within which the discrimination potential was maximized [3]. The setup has been parallelized to increase throughput and to become able to test a large number of coating chemistries per day. Due to the modular assembly of our setups, not only model surfaces and thin organic films, but also practical coatings can be tested.

[1] M. Alles, A. Rosenhahn, *Biofouling.* **2015,** 31, 469–480.

[2] MP. Schultz, *et al*., *Biofouling.* **2000,** 15, 243-251.

[3] K. Nolte, J. Schwarze, A. Rosenhahn *Biofouling.* **2017,** in press

10:40am **BI-MoM8 Coatings with Amphiphilic Surfaces Via Self-Stratification for Marine Fouling-Release Applications**, ***Dean Webster***, *T. Galhenage, S. Stafslien, L. Vanderwal*, North Dakota State University

Due to the complexity of adhesion mechanisms of marine life to surfaces, it is becoming apparent that combating biofouling will require coatings having complex surfaces. Specifically, coatings having mixed hydrophobic and hydrophilic surface domains are being shown to be able to mitigate the adhesion of a broader variety of marine organisms than can the silicone elastomer fouling-release coatings. Since it is also desirable to have a coating that can adhere well to a variety of substrates and stand up to occasional cleaning, a tough coating system is needed.

The incorporation of a low surface energy polymer such as a siloxane into a robust coating system such as a polyurethane results in stratification of the low surface energy component to the surface. By chemically binding hydrophilic groups to the siloxane, both functional groups stratify leading to a polyurethane coating having amphiphilic character on the surface. By varying the molecular parameters of the hydrophobic and hydrophilic components, the surface composition can be tuned to achieve a range of fouling-release properties when characterized using a broad variety of marine organisms. Different architectures of the reactive amphiphilic component have been explored including block and graft copolymers as well as dual-functionalized prepolymers.

11:00am **BI-MoM9 Zero-Energy Flux Recovery in Biofouled Liquid Gated Membranes**, *J.C. Overton*, ***Caitlin Howell***, University of Maine

Membranes coated with antifouling immobilized liquid layers have been recently shown to permit filtration while reducing surface fouling. In this work, we test the ability of liquid gated membranes created with expanded polytetrafluoroethylene and perfluorinated liquids to reduce the buildup of internal pore fouling using whey protein, an extremely challenging biological foulant. We find no differences in the decrease of flux or rate of fouling between coated and uncoated membranes in a dead-end filtration setup. However, upon stopping flow for 15-30 minutes, up to 70% of the original flux can be recovered with no additional energy input. This cycle can be repeated multiple times, with approximately 5% decrease in flux recovery each time. We use standard fouling equations and light microscopy to demonstrate that this zero-energy recovery may occur within the pores of the membrane due to the refilling of the pore with lubricating liquid, pushing the proteins off the pore walls. This work could have important applications in filtration processes with high fouling rates, reducing costs associated with standard chemical or physical cleaning methods.

11:20am **BI-MoM10 Stimuli Responsive Polymers in Biofouling and Bioadhesion**, ***Gabriel Lopez***, University of New Mexico **INVITED**

This talk will review work by the Lopez lab and its collaborators on the role of stimuli-responsive polymers in processes associated with biopolymer adsorption, biofouling and bioadhesion. Wikipedia currently defines stimuli-responsive (or “smart”) polymers as those that change their shape or properties “according to the environment they are in.” From this perspective, almost any polymer in solution that adsorbs to an interface placed in its proximity can be thought of as a stimuli-responsive polymer. In the present context, a less trivial distinction includes polymeric systems that are sensitive to external fields (e.g., thermal, stress, optical, electric) in a way as to dramatically affect tendency for adsorption or adhesion. Such polymeric systems include synthetic polymers comprising engineered interfaces with biologically relevant aqueous phases (brushes, solution and vacuum deposited films, gels) and biopolymers (proteins) in aqueous phases. These systems and their ability to dramatically influence adsorption, attachment and adhesion are of potential use in a wide range of biotechnological, biomedical, aquatic, marine and food production applications including processes such as separations, assays, controlled delivery, cell culture, packaging, energy transfer and transportation.

## Spectroscopic Ellipsometry Focus Topic
## Room: 9 - Session EL+AS+EM+TF-MoM

## Application of SE for the Characterization of Thin Films and Nanostructures
**Moderator:** Tino Hofmann, University of North Carolina at Charlotte

8:20am **EL+AS+EM+TF-MoM1 Ultra-thin Plasmonic Metal Nitrides: Optical Properties and Applications**, ***Alexandra Boltasseva***, Purdue University **INVITED**

Transition metal nitrides (e.g. TiN, ZrN) have emerged as promising plasmonic materials due to their refractory properties and good metallic properties in the visible and near infrared regions. Due to their high melting point, they may be suitable for high temperature nanophotonic applications. We have performed comprehensive studies of the temperature induced deviations to the dielectric function in TiN thin films. The studies were conducted on 30 nm, 50 nm, and 200 nm TiN films on sapphire substrates at temperatures up to 900 0C in the wavelength range 350-2000 nm using a custom built in-situ high temperature ellipsometry setup. The results were fitted with a Drude-Lorentz model consisting of one Drude oscillator and 2 Lorentz oscillators. As the temperature is elevated, the real and imaginary parts both begin to degrade. However, the deviations to the optical properties of TiN are significantly smaller compared to its noble metal counterparts, with no structural degradation in the TiN films. In addition to high temperature applications, TiN could also be a potential material platform for investigating light-matter interactions at the nanoscale, since high quality, continuous films of TiN can be grown on substrates such as MgO and c-sapphire down to just a few monolayers. Ultrathin TiN films with thicknesses of 2, 4, 6, 8, and 10 nm were grown on MgOusing DC reactive magnetron sputtering, resulting in high quality films with low roughness. The changes in the linear optical properties were investigated using variable angle spectroscopic ellipsometry at angles of 50° and 70° for wavelengths from 400 nm to 2000 nm. A Drude-Lorentz model consisting of one Drude oscillator and one Lorentz oscillator was used to fit the measurements. As the thickness decreased, an increase in the losses and a decrease in the plasma frequency was observed. However, the films remained highly metallic even at 2nm, demonstrating that they could be used for nanophotonicapplications, including nonlinear optical devices and actively tunable plasmonic devices.

9:00am **EL+AS+EM+TF-MoM3 Magnetron Sputtering of TiN Coatings: Optical Monitoring of the Growth Process by Means of Spectroscopic Ellipsometry**, ***Jiri Bulir***, *J. More Chevalier, L. Fekete, J. Remiasova, M. Vondracek, M. Novotny, J. Lancok*, Institute of Physics ASCR, Czech Republic

The plasmonic applications requires search for novel materials with metal-like optical properties and low optical losses. Transition metal nitrides such as TiN, TaN, ZrN, HfN, NbN exhibit metallic properties depending on concentration of free-carrier of charge. Their plasmonic properties can be tuned by deposition parameters controlling the film structure and the stechiometry.

In this work, we deal with study of growth process of TiN films. The films are grown by RF magnetron sputtering on fused silica, silicon and MgO substrates at substrate temperature ranging from 20°C to 600°C. The growth process is monitored using in-situ spectral ellipsometer in spectral range from 245 to 1690 nm. The ellipsometric data, which are obtained during the deposition process, are attentively analysed using mathematical models based on Drude-Lorentz oscillators.

The Lorentz oscillators are used for description of interband transition in ultraviolet and visible spectral range, whereas the Drude oscillator describes the free-electron behavior in the infrared spectral range. We show that the free-electron behavior is affected by thickness of the ultrathin coatings due to electron scattering effects at the interfaces. Number of physical parameters such as free-electron concentration, Drude relaxation time and electrical conductivity is estimated at each stage of the deposition process by analysis of dielectric functions using the mentioned model. The resulting evolution of the electrotransport properties during the TiN film growth is presented. Special attention is devoted to the initial nucleation stage when the free-electron behaviour is significantly influenced by the interface between the substrate and the TiN film. Based on evolution of electrotransport properties, we discuss differences between polycrystalline growth of TiN film on Si and fused silica substrates and epitaxial growth on MgO substrates.

The accomplished TiN coatings are analyzed using infrared ellipsometer operating in spectral range from 1.7μm to 30μm where the optical constants are infuenced most importantly by free-electron behaviour. The obtained results are compared with those obtained by the in-situ ellipsometer. Special attention is focused on scattering of free electrons at grain boundaries and at the TiN layer interfaces. The estimated parameters are correlated with structure changes such as grain coarsening and surface morphology. The crystallinity is analysed by X-ray Difractometry. The surface morphology of the completed coatings is studied using Atomic Force Microscopy and Scanning Electron Microscopy. The TiN film stechiometry is estimated by X-ray Photoemission Spectroscopy.

9:20am **EL+AS+EM+TF-MoM4 Variable Temperatures Spectroscopic Ellipsometry Study of the Optical Properties of InAlN/GaN Grown on Sapphire**, *Y. Liang,* Guangxi University, China, *H.G. Gu,* Huazhong University of Science and Technology, China, *J. Xue,* Xidian University, China, ***Chuanwei Zhang,*** Huazhong University of Science and Technology, China, *Q. Li,* Guangxi University, China, *Y. Hao,* Xidian University, China, *S.Y. Liu,* Huazhong University of Science and Technology, China, *Q. Yang, L. Wan, Z.C. Feng,* Guangxi University, China

Indium aluminum nitride (InAlN), a prospective material for lattice matched confinement layer, possesses the potential to improve the reliability and performance of high electron mobility transistors (HEMTs).[1] One of the important advantages of InAlN alloy is the possibility of growing in-plane lattice-matched to GaN for an indium content of around 17%. However, the bandgap we expected is hindered by the growth of high-quality InAlN films due to the phase separation and nonuniform composition distribution.[1-2]

In this work, InAlN/GaN heterostructures, grown by pulsed metal organic chemical vapor deposition (PMOCVD) on c-plane sapphire substrates, were investigated by a dual rotating-compensator Mueller matrix ellipsometer (ME-L ellipsometer, Wuhan Eoptics Technology Co. Ltd., China). The experimental data ($\Psi$ and $\Delta$), covering the wavelength ($\lambda$) range from 193 nm up to 1700 nm at 1 nm step or energy (E) from 0.73 eV to 6.43 eV, were obtained by variable temperatures spectroscopic ellipsometric (VTSE) in three angles (50°, 55° and 60°). The Eoptics software was utilized to fit VTSE data using Tauc-Lorentz multiple oscillator modes. By analyzing the fitting results, the optical constants of the InAlN at variable temperatures (25℃-600℃) were obtained. The peak value of the refractive index increases from 269 nm to 284 nm with increasing temperature. The bandgaps are 4.57 eV and 4.35 eV at the temperature 25℃and 600℃, respectively. These results demonstrated that InAlN/GaN has a high thermal stability, scilicet no significant performance degradation in high temperature environment.

Reference

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[2] JunShuai Xue, JinCheng Zhang, Yue Hao, Investigation of TMIn pulse duration effect on the properties of InAlN/GaN heterostructures grown on sapphire by pulsed metal organic chemical vapor deposition, Journal of Crystal Growth 401, 661 (2014).

9:40am **EL+AS+EM+TF-MoM5 Optical Properties of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ Double Perovskite Studied by Spectroscopic Ellipsometry**, ***Honggang Gu***, *S.R. Li, B.K. Song, J. Tang, S.Y. Liu,* Huazhong University of Science and Technology, China

During the past several years, the organic-inorganic lead halide perovskites ($APbX_3$, $A = CH_3NH_3$ or $NH_2CHNH_2$, X = Cl, Br, or I) have been promising materials for photovoltaic, photoelectric -detecting and light-emitting devices due to their outstanding photoelectric properties, such as broad absorption range, high quantum efficiency, ultrafast charge generation, high charge carrier mobility and long charge carrier lifetime and diffusion length. However, there are two remaining challenges that need to be addressed in order to apply these materials to photoelectric productions, namely the compound stability and the presence of lead. Most recently, lead-free metal halide double perovskites, such as $Cs_2AgBiCl_6$ and $Cs_2AgInCl_6$, have attracted extensive attention because of their nontoxicity and relative air-stability. In the study and application of these perovskite materials, the knowledge of their optical properties, such as the bandgap and the basic optical constants, is of great importance to predict the photoelectric characteristics and dig the potential of the materials.

Spectroscopic ellipsometry (SE) has been developed as a powerful tool to characterize the optical properties as well as structure parameters of novel materials, thin films and nanostructures. In this work, we study the optical properties of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ perovskites by a spectroscopic ellipsometer (ME-L ellipsometer, Wuhan Eoptics Technology Co., Wuhan, China). The refractive index and the extinction coefficient of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ with different composition coefficient $x$ of bismuth are determined by the ellipsometer over the wavelength range of 250-1000nm. We find that the presence of bismuth introduces two critical points in the optical constant spectra of the perovskites, i.e., 315nm and 382nm in the refractive index spectra and 300nm and 375nm in the extinction coefficient spectra, respectively. Moreover, there is a red shift in the bandgaps and significant increase in both the refractive index and the extinction coefficient with the increase of composition coefficient $x$ of bismuth.

10:00am **EL+AS+EM+TF-MoM6 Charge Carrier Dynamics of Aluminum-doped Zinc Oxide Deposited by Spatial Atomic Layer Deposition**, ***Daniel Fullager***, *G. Boreman, T. Hofmann,* University of North Carolina at Charlotte, *C.R. Ellinger,* Eastman Kodak Company

Transparent conductors for displays, backplanes, touchscreens and other electronic devices are an area of active research and development; in this manner, aluminum-doped zinc oxide (AZO) has shown promise as an ITO replacement for some applications. Although there have been numerous reports on the optical properties and electrical conductivity of AZO, there has not yet been a Kramers-Kronig consistent dispersion model fully describing the charge carrier dynamics. In this presentation, we will report on the model dielectric function of AZO from the combination of UV-Vis and IR spectroscopic ellipsometry. A model dielectric function that describes the optical response over this wide spectral range will be presented and discussed. In particular, we will present a comparison between the commonly used extended Drude models and the dielectric function developed here in light of results obtained from density functional theory calculations.

The AZO films analyzed in this study were deposited using a spatial atomic layer deposition (SALD) process. While AZO can be deposited by several techniques, including sputtering, chemical vapor deposition (CVD), and atomic layer deposition (ALD), ALD does allow for the greatest ability to control the aluminum-doping level of AZO. However, the range of substrate sizes and form factors addressable by traditional chamber ALD are limited. Conversely, spatial ALD (SALD) is an atmospheric pressure, roll-compatible ALD process that enables the materials property control of ALD to be translated into a wider range of applications spaces. Furthermore, the use of selective area deposition in a “patterned-by-printing” approach enables the high-quality AZO deposited by SALD to be easily patterned, offering an integrated and facile path for manufacturing optical and electronic devices.

10:40am **EL+AS+EM+TF-MoM8 Broad Range Ellipsometry Shining Light onto Multiphase Plasmonic Nanoparticles Synthesis, Properties and Functionality**, ***Maria Losurdo***, CNR-NANOTEC, Italy **INVITED**

How rich are the physics, interface chemistry and optical properties associated with the surface plasmons of metal nanostructures and their potential for manipulating light at the nanoscale! For many technological applications nanoparticles (NPs) are supported on a substrate, and at the nanoscale, interaction and interfaces with the support become very important. We have demonstrated that the substrate/NPs interaction is the key to engineering not only the shape but also the crystalline phase of NPs.

This contribution will present and explore fundamental and applied aspects of multiphase core-shell plasmonic NPs supported on substrates of technological interest using various diagnostic tools, which comprise: (i) spectroscopic ellipsometry spanning the THz, IR, visible, and UV wavelength ranges, (ii) variable angle Muller Matrix ellipsometry to qualify size effects on anisotropy and depolarization of samples, (iii) *in-situreal-time* spectroscopic ellipsometry to understand growth and tailor particle size which ultimately controls the plasmon resonance, and (iv) various imaging and microscopies techniques to elucidate the interplay between the nanostructure of multiphase nanoparticle and their functionality.

The case studies involve liquid-shell/solid-core plasmonic NPs (Ga, Ga/Mg), plasmon-catalytic core/shell Ga/Pd and plasmon-magnetic Ni/Ga NPs supported on various substrates (glass, plastics, sapphire) that control their crystalline phases.

We will start with a description of the *real-time* ellipsometry capabilities in monitoring the growth of those multiphase core/shell NPs to detect the formation of the various phases in situ and to control the resulting plasmon resonance.

The discussion then will shifts to a description of fundamental of thermodynamics of substrate supported multiphase NPs and how their growth dynamics is controlled by the interface energies, and how those new phenomena can be highlighted by real-time ellipsometry.

Ex-situ corroborating measurements of Mueller-matrix ellipsometry and hyperspectral cathodoluminescence spectroscopy and imaging will be presented to discuss phenomena of depolarization and of interaction of NPs resulting from the self-assembly.

Finally, since those NPs enable active plasmonics, we demonstrate the implications of the multi-phase nature of NPs, as well as solid-liquid phase coexistence on the plasmon resonance (LSPR) of supported NPs and on its exploitation to follow in real time phenomena in their application in catalysis (hydrogen storage and sensing) and optomagnetism and possible future directions.

*The contribution of the H2020 European programme under the project TWINFUSYON (GA692034) is acknowledged*

11:20am **EL+AS+EM+TF-MoM10 Use of Evolutionary Algorithms for Ellipsometry Model Development and Validation using Eureqa**, ***Neil Murphy***, Air Force Research Laboratory, *L. Sun*, General Dynamics Information Technology, *J.G. Jones*, Air Force Research Laboratory, *J.T. Grant*, Azimuth Corporation

Eureqa, developed by Nutonian Inc., is a proprietary modeling engine based on automated evolutionary algorithms. In this study, we utilized Eureqa to parameterize both the amplitude and phase difference data for reactively sputtered thin films. Specifically, evolutionary algorithms are used to develop and validate models for fitting raw ellipsometric data for a variety of optical materials including $SiO_2$, $Ta_2O_5$, and Aluminum Zinc Oxide. These films, deposited using pulsed DC magnetron sputtering, were deposited on both silicon and fused quartz substrates, and measured using a J.A. Woollam VASE system. The resulting models are then compared to traditional models that are currently utilized to fit the candidate materials systems.

11:40am **EL+AS+EM+TF-MoM11 Excitonic Effects on the Optical Properties of Thin ZnO Films on Different Substrates**, ***Nuwanjula Samarasingha***, *Z. Yoder, S. Zollner*, New Mexico State University, *D. Pal, A. Mathur, A. Singh, R. Singh, S. Chattopadhyay*, Indian Institute of Technology Indore, India

The presence of excitonic features in the optical constants of bulk semiconductors and insulators has been known for many years. In Si, Ge, and GaAs, the $E_1$ critical points are strongly enhanced by two-dimensional excitons. Three-dimensional excitons have been seen in ellipsometry spectra for GaP and Ge. In addition to these semiconductors, wide band gap materials like ZnO exhibit strong excitonic features in the dielectric function (ε) which is directly related to the electronic band structure. The top valence band at the Γ point in the Brillouin zone is split into three bands by spin orbit and crystal field splitting. The corresponding free exciton transitions between the lowest conduction band and these three valence bands are denoted by A, C ($\Gamma_7$ symmetry) and B ($\Gamma_9$ symmetry). The transition from the B subband is forbidden for light polarized parallel to the optical axis (extraordinary dielectric function). ZnO is attractive for optoelectronic device applications due to its large excitonic binding energy of 60 meV at room temperature.The influence of this excitonic absorption on ε was described by Tanguy [1].

Here we investigate the behavior of excitons in c-oriented ZnO thin films grown on Si (smaller band gap than ZnO) and $SiO_2$ (larger band gap than ZnO) substrates using variable angle spectroscopic ellipsometry and FTIR ellipsometry. We also performed X-ray diffraction (XRD), X-ray reflectivity (XRR), and atomic force microscopy (AFM) to characterize the structural properties of our ZnO films.

In a thin epitaxial layer on a substrate with a different band gap, the wave functions of the electron and hole are strongly modified. In ZnO (band gap 3.37 eV) grown on a large-gap $SiO_2$ substrate (type-I quantum well), both the electron and the hole are confined, which leads to an increase in the dipole overlap matrix element. Therefore, the real and imaginary part of ε of thin ZnO layers on $SiO_2$ are much larger than in the bulk and increase monotonically with decreasing thickness.

On the other hand, in a staggered type-II quantum well (ZnO on Si), either the electron is confined, or the hole, but not both. Therefore, the overlap dipole matrix element is strongly reduced. Therefore, ε of thin ZnO layers on Si is much smaller than in the bulk and decreases monotonically with decreasing thickness. We will fit our ellipsometric spectra by describing the dielectric function of ZnO using the Tanguy model [1]. We will analyze the dependence of the excitonic Tanguy parameters on quantum well thickness and substrate material.

Reference:

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## 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$_2$YZ inverse-Heusler, 576 X$_2$YZ 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 $\mu_B$/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.

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11:40am **EM+MI+TF-MoM11 Formation of the Epitaxial MgO/Full-Heusler $Co_2MnSi$ 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 $Co_2MnSi$ has received considerable attention as it is quite stable ($\Delta H_F$ = -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/$Co_2MnSi$(001) interface has been studied *in-situ* using X-ray photoelectron spectroscopy (XPS). $Co_2MnSi$ layers were grown on Cr-buffered MgO(001) substrates by coevaporation of elemental sources in ultrahigh vacuum while MgO was grown on the $Co_2MnSi$ layers using e-beam evaporation of stoichiometric source material. It was found that partial oxidation of the $Co_2MnSi$ 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/$Co_2MnSi$ interface with composition significantly different from the unoxidized $Co_2MnSi$ surface. In addition, Mn and Si oxides at the MgO/$Co_2MnSi$ 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/$Co_2MnSi$ MTJs which were observed to be highly sensitive to post-growth annealing temperature.

## MEMS and NEMS Group
## Room: 24 - Session MN+BI+NS-MoM

## Feature Session: Large Scale Integration of Nanosensors

**Moderators:** Wayne Hiebert, National Institute for Nanotechnology, Canada, Robert Davis, Brigham Young University

8:20am **MN+BI+NS-MoM1 Large Scale Integration: A Not-so-simple Cure for Loneliness of Silicon Nanoresonators**, ***Sébastien Hentz***, Cea Leti, France **INVITED**

After two decades of pioneering work, Nano Electro Mechanical Systems are only starting to fulfil (some) of their huge promises, in particular for sensing. A few start-up companies have been created in the last few years, but NEMS are still far from the industrial success of their micro- counterparts. Among others, one reason is the increasing difficulty to interface the "real-world" quantities to sense with the extremely small size of nanomechanical resonators. An easy to understand example of this is mass sensing: there is huge size mismatch between the NEMS capture cross section (in the $\mu m^2$ range) and an actual particle beam size that one can produce (in the mm to $10mm^2$ range). Most of the particles to detect are lost. Industrial applications may require the use of large arrays comprising from 10's to 10000's NEMS.

LETI has been working on nanomechanical resonators for a number of applications in the last ten years and have been pioneering their fabrication with Very Large Scale Integration processes. State of the art performance (signal to background ratio, signal to noise ratio, frequency stability...) has been reached with single silicon resonators and specific transduction means adapted to VLSI technologies. The real strength of VLSI though, as evidenced every day by microprocessor fabrication is the possibility to process a large number of devices operating in sync with great reproducibility and control.

We investigated several types of NEMS arrays in the past at LETI. Arrays comprising typically a few 1000 resonators all connected in parallel for gas sensing have been demonstrated. Smaller arrays with the ability to weigh and localize single particles via frequency addressing have been tested too for mass spectrometry applications. LETI has also been pioneering NEMS co-integration with CMOS in the last decade or so and several technologies have been explored. We took advantage of this know-how to fabricate large and dense arrays of NEMS-CMOS arrays for mass sensing applications.

9:00am **MN+BI+NS-MoM3 Nanomechanical Sensors (MSS, AMA) Toward IoT Olfactory Sensor System**, ***Genki Yoshikawa***, National Institute for Materials Science, Japan **INVITED**

Owing to their intrinsic versatility, nanomechanical sensors have potential to cover a wide range of olfactory sensing applications in various fields including food, agriculture, medicine, security, and environment. Based on the newly developed platform "Membrane-type Surface stress Sensor (MSS)," we are now trying to realize useful nanomechanical sensor systems which can fulfill the practical requirements, such as portability, low-cost, ease of use, in addition to the basic specifications, e.g. high sensitivity and selectivity. While the MSS provides a practical sensing element, a consumer mobile/IoT sensor system requires further optimization and integration of lots of components including receptor layers, hardware including electronics and sample handling, multidimensional data analysis, and precise calibration for high reproducibility. To establish a de facto standard for odor analysis and sensor systems employing the nanomechanical MSS technology, the "MSS Alliance" was launched jointly with companies and a university. In addition, "Aero-Thermo-Dynamic Mass Analysis (AMA)," which we have recently developed, will provide another approach to characterizing gases by directly measuring molecular weight in ambient condition without a vacuum or ionization. In this talk, the overview of the MSS, AMA, and the related technologies ranging from the optimization scheme of the sensor chip to system level developments will be presented.

9:40am **MN+BI+NS-MoM5 Micro-Gas Chromatography Linked with Nano-optomechanical Systems for Breath Analysis**, ***Khulud Almutairi***, University of Alberta, Canada, *W.K. Hiebert*, National Institute for Nanotechnology, Canada

One of the applications of microfabrication and nanofabrication technologies is fabricating a micro-Gas Chromatography (GC) on a chip. The miniaturized GC system is designed for the rapid determination of volatile organic compounds (VOCs) that can be used in remote locations with low consumptions and cost of utilization. It was reported that specific VOCs can be found in exhaled breath sample from patients suffering from lung cancer [1]. Therefore, designing a µGC device can help in separating and analyzing VOCs that comes from exhaled breath samples, such as acetone, benzene and toluene.

Our group has reported that connecting Nano-optomechanical systems (NOMS) to Gas Chromatography can enhance the detection sensitivity limit of VOCs up to 1 ppb [2]. This presentation will feature our first efforts in connecting µGC with NOMS for higher sensitivity and responsivity. In particular, we will discuss our NOMS sensor chips with microheaters for localized control of sensor temperature. One of our goals is to move toward large scale integration of GC analysis by simultaneously sensing at multiple temperatures.

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[2] Venkatasubramanian, Anandram, Vincent TK Sauer, Swapan K. Roy, Mike Xia, David S. Wishart, and Wayne K. Hiebert. "Nano-optomechanical systems for gas chromatography." *Nano Letters* 16, no. 11 (2016): 6975-6981.

10:00am **MN+BI+NS-MoM6 Micro Chladni Figures and Multimode Manipulation of Breast Cancer Cells in Liquid**, ***Hao Jia***, *H. Tang*, Case Western Reserve University, *X. Liu, H. Liu*, Northwestern University, *P.X.-L. Feng*, Case Western Reserve University

Non-invasive, microscale positioning of delicate biological cells can foster fundamental research involving probing cellular properties and controlling cellular behaviors and interactions [1-3], which lead to a multitude of applications, such as disease screening, tissue engineering, *etc*.

Here we demonstrate that microscale manipulation of breast cancer cells can be achieved in a fast and non-invasive manner through exploiting multimode micromechanical systems. We design edge-clamped diaphragm resonators (~300µm in length scale) and piezoelectrically excite their mechanical resonances (within 50–500 kHz) in fluidic environment. The transverse vibrations induce localized, microscale hydrodynamic flow that can aggregate microbeads (3.6µm-diameter) on device surfaces into a variety of one- and two-dimensional (1D and 2D) 'Chladni figures' [4] (optical images in Fig.1a & b). This phenomenon allows us to further manipulate single or a group of breast cancer cells (MDA-MB-231, 15µm-diameter), in both 1D and 2D fashions, at a speed of ~4µm/s (fluorescent images in Fig. 1a & b). By simply programming the piezoelectric excitation frequency, we achieve dynamic control of cancer cell spatial distributions, switching between mode patterns.

We further demonstrate that such multimode resonator platform can facilitate cellular-level biological studies, such as evaluating cellular adhesive interactions and its connection with cancer biomarker (*e.g.*, CD44). As shown in Fig.2, by exploiting the ‘Chladni figure’ phenomenon, and carefully selecting 2 resonance modes of a square diaphragm, *e.g.*, Mode (1,1) and Mode (3,3), a controlled number of MDA-MB-231 cells can be quickly manipulated into single cluster and then forced to break as the excitation voltage of Mode (3,3) gradually increases. Cancer cells with CD44 gene knocked out by CRYSPR technology are named as $CD44^-$ cells, while those with CD44 gene maintained named as $CD44^+$ (control) cells. The break of $CD44^-$ cell cluster after $0.8V_{pp}$ in Fig. 2 indicates that they form much weaker adhesive interactions than $CD44^+$ cells do, which indicates that CD44 plays a significant role in the metastatic breast cancer cell clustering.

[1] E.E. Hui, *et al.*, PNAS **104**, 2007.

[2] H. Zhang, *et al.*, J. R. Soc. Interface **5**, 2008.

[3] X. Ding, *et al.*, PNAS**109**, 2012.

[4] E.F.F. Chladni, *Entdeckungen über die Theory des Klanges*,1787.

10:40am **MN+BI+NS-MoM8 Microfabrication and Assembly Processes for Integrating Microelectrode Arrays into Tissue-Engineered Scaffolds for Novel Nerve Interfaces**, ***Jack Judy***, *C. Kuliasha, P. Rustogi, S. Natt, B. Spearman, S. Mohini, J.B. Graham, E.W. Atkinson, E.A. Nunamaker, K.J. Otto, C.E. Schmidt,* University of Florida **INVITED**

To advance fundamental understanding and develop therapies for neurological disease or injury, microfabricated implantable electrode arrays have been designed and manufactured to stimulate and record neural activity. The materials in these implants, as well as the processes used to integrate them together, must be carefully selected to maximize biocompatibility, device performance, and overall reliability. For upper-limb amputees, nerves are a promising neural-interface target to control sophisticated robotic limbs. Recent advances have shown that nerve stimulation can provide natural sensory feedback. In contrast, it is currently not possible to extract large-scale, high-resolution, and reliable movement-intent signals from nerves. To provide rapid and precise limb control and elicit high-resolution sensory percepts, a nerve interface needs many independent motor and sensory channels. Unfortunately, all existing non-invasive and non-regenerative nerve interfaces grossly under-sample the heterogeneous population of efferent and afferent axons. Although tissue engineering, nerve regeneration, and implantable neural-electronic interfaces are individually well-established fields, the concept of merging these fields to create scalable, and high-performance neural interfaces has not been extensively explored. To overcome the scalability challenge, we present a novel approach. Specifically, we describe a hybrid tissue-engineered electronic nerve interface (TEENI), which consists of multi-electrode polyimide-based “threads” embedded into a biodegradable hydrogel composite scaffold that is sutured to the ends of a transected nerve. Single or multiple thread sets can be incorporated in the hydrogel to enable the TEENI implant to comprehensively engage with the nerve. These polyimide threads will be fully enveloped and held precisely in position during implantation by the hydrogel scaffold, which has properties optimized to reduce foreign-body response. Eventually, the hydrogel will degrade and be replaced with regrown and maturing axons. Since the TEENI approach is scalable to high channel counts over the nerve volume, we believe TEENI nerve interfaces are well positioned to comprehensively capture movement-intent information and impart sensory-feedback information so that upper-limb amputees can get the most out of their prosthetic limbs.

11:20am **MN+BI+NS-MoM10 Magnetically Actuated Synthetic Cilia for Microfluidics**, ***Peter Hesketh***, *S.K.G. Hanasoge, M. Ballard,* Georgia Institute of Technology*, M. Erickson,* University of Georgia*, A. Alexeev*, Georgia Institute of Technology **INVITED**

Many bacteria use cilia for swimming, sensing and signal transduction. These functions are achieved by manipulating the fluid around the cilia with continuous and synchronised asymmetric beating patterns . We have fabricated arrays of synthetic cilia using thin film deposition of NiFe thin films. The cilia are able to manipulate fluid in these creeping flow regimes by creating an asymmetry in the forward and recovery strokes. We propose to use artificial cilia in microfluidic devices to perform different functions including mixing, fluid transport, and particle capture.

We use a simple rotating magnet to actuate the cilia array and observe a large asymmetry in the bending pattern of these cilia in the oscillation cycle. We analyze the asymmetric strokes of the cilia by imaging from the side view and quantify the asymmetry between forward and recovery strokes as a function of drive frequency. These asymmetric oscillations are important in creating any microfluidic transport phenomenon such as pumping, mixing and capture in a microchannel as demonstrated in this work. Computational modeling was also used to simulate the motion of the cilia over a broader range of design parameters. We show the dependence of the ciliary performance on several non-dimensional numbers based on the balance of magnetic, viscous and elastic forces acting on the cilia.

The motivation for this work is to improve the quality of sampling for the detection of bacteria and virus in food. Detecting low concentrations of bacteria in food samples is a challenge. The pre-concentration and separation of the target bacteria from the food matrix can be enhanced using improved fluid handling. We demonstrate particle capture with cilia, by functionalizing the surface of the cilia with streptavidin protein and capturing biotin labelled particles on its surface. The functionalized cilia are incorporated inside a microchannel and biotin labelled particles are introduced into array of the cilia. Likewise, these artificial cilia find varied application in many lab on a chip devices where active fluid transport is needed.

## Plasma Science and Technology Division
## Room: 21 - Session PS+AS+SE-MoM

## Atmospheric Pressure Plasmas

**Moderators:** Olivier Guaitella, Ecole Polytechnique - CNRS, France, Seiji Samukawa, Tohoku Univeversity, AIST, Japan

8:20am **PS+AS+SE-MoM1 Study of Atmospheric-pressure kHz Multi-jet Plasma System**, ***Vladimir Milosavljevic***, *J. Lalor, L. Scally, P.J. Cullen*, Dublin Institute of Technology, Ireland

Non thermal plasmas can be generated in laboratory conditions using generic, readily available and easily sourced components. Examples include glass tubing, copper or stainless wire electrodes, metal mesh, plastic enclosures, and step-up transformer based power supplies. Such sources, although effective, may not offer optimised conditions or efficiencies. In many cases they may not sustain extended operation due to excess thermal and electrical breakdown. Second-generation laboratory apparatus and scaled up designs involve selected materials, custom machined components, electrodes based on calculated requirements, and suitably designed or sourced power supplies. These assemblies will offer a more accurate theoretical and empirical view of the plasma performance. The inclusion of a material selection software tool for the rational selection of engineering materials can provide detailed information relating to the mechanical thermal and electric properties. Developing a non-thermal atmospheric plasma source involves three important factors for material selection. Firstly the application and operating conditions of the design needs to be examined; is it to be handheld, exposed to ambient air or contained in an enclosure. For many plasma sources, certain polymers offer an ideal material, for other configurations, composites or metals may be best. Secondly, does the source need to facilitate a controllable environment in which to generate the plasma, in other words, is it necessary to purge or evacuate the enclosure in order to accurately control the gas chemistry, if this is the case, a choice of material for this housing and containment area must be considered. The third factor is the material selection for the conducting elements, namely the cables, electrodes and grounding components. Typical electrode metals include copper, aluminium, brass and stainless steel.

In this work 12 circular plasma jets are presented. They are designed and built in-house, and power up with a single phase generator of 10-30 kV, at 10-100 kHz that powers up to 2 kW. Voltage-current measurements and optical emission spectroscopy (OES) are applied for optimization of transient discharges operated for several different gas chemistry at atmospheric pressure. The influence of applied voltage, frequency, gas flow rate and gas chemistry in relation with the OES signal, plasma plume formulation, gas velocity and electrical properties of plasma jets are the objectives of this study.

This work was funded under the ’PlasmaGrain’ project funded by the SFI, Republic of Ireland.

8:40am **PS+AS+SE-MoM2 Synthesis of Nitrates by Atmospheric Microplasma Over Water : Effect of the Experimental Parameters and Intermediate Species**, ***Nicolas Maira***, *C. De Vos, F. Reniers*, Université Libre de Bruxelles, Belgium

Nowadays, nitrates are used mainly as fertilizers in agriculture. They are produced by the combination of the Haber-Bosch and Ostwald process. Industry, throughout the years, has increasingly optimized the energetic yield of this synthesis. Nevertheless, this method requires the use of a hydrogen source, essentially extracted from fossil fuel. Moreover, nitrates synthesized in colossal plant factories have to be shipped to the end-user. However, in some applications such as hydroponics or urban agriculture, the local production of pure nitrates fertilizers directly available in the flowing water feeding system would be of great interest.

In this study, the same philosophy as for the ozone process is applied: taking advantage of the composition of natural air in order to synthesize nitrates directly in a solution [1]. The mechanism of formation of nitrates using an atmospheric microplasma discharge operating in air or in argon in an open air environment is investigated. The effect of the treatment time, the discharge current and power, the water surface – capillary distance, and the solution pH on the formation of nitrogen oxides in the gas phase and in solution is studied. The liquid phase is analyzed by Ionic Chromatography (IC), UV-visible spectrometry (UV-vis) and pH-metry, whereas the gas phase is probed by Optical Emission Spectroscopy (OES) and atmospheric Mass Spectrometry (MS).

The total amount of $NO_x$ formed in a solution shows a linear trend with the total charge injected into the plasma with however different slopes for nitrites ($NO_2^-$) and nitrates ($NO_3^-$). The reaction mechanism involves the formation of gas phase NO, as evidenced by OES. It is known that the synthesis of nitrates is pH-dependent [2]. In an acidic solution with a pH below 3, the formation of nitrates is favored whereas a higher pH allows the formation of nitrites which are oxidized in nitrates after the treatment. The transformation of nitrites into nitrates after plasma synthesis is monitored by IC during time and seems to follow a logarithmic trend. The performed experiments allow the determination of the amount of energy required to form a mole of nitrate in this set-up.

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[2] Machala Z., Tarabova B., Hensel K., Spetlikova E., Sikurova L., Lukes P. Formation of ROS and RNS in water electro-sprayed through transient spark discharge in air and their bactericidal effects, *Plasma Processes and Polymers*, 10, 649-659, **2013**.

9:00am **PS+AS+SE-MoM3 Plasma Catalysis for $CO_2$ and $CH_4$ Conversion at Atmospheric Pressure**, *A. Ozkan, S. Chorfi, L. Brune, T. Visart de Bocarmé, **François Reniers***, Université Libre de Bruxelles, Belgium

The field of plasma-catalysis, i.e. combining a plasma process and a catalyst, either inside the plasma or in its post-discharge is gaining importance for the conversion of $CO_2$ and $CH_4$ mixtures. Indeed, the combination of plasma and catalysis could not only increase the conversion of these gases, but also orient the reaction(s) towards the synthesis of valuable molecules.

This paper will present first the main factors that influence the conversion and the energy efficiency for the reduction of $CO_2$ using an atmospheric pressure dielectric barrier discharge. Second, an alumina supported catalyst will be added between the electrodes and its effects on the conversion of pure $CO_2$, pure $CH_4$ and $CO_2/CH_4$ mixtures will be presented. Ni, Co, Cu have been tested, as well as various loadings of Ni.

The conversion is studied by atmospheric mass spectrometry, and the chemical identification of the end products was obtained either by mass spectrometry or gas chromatography.

It is shown that the frequency, the pulse mode, the dielectric nature and thickness strongly influence the conversion and energy efficiency of the reaction, whereas the residence time and the power injected into the discharge modify the conversion[1]. An increase in the Ni loadings leads to an increase in conversion of both $CO_2$ and $CH_4$. If CO and $H_2$, starting molecules for more complex organic chemistry, are always the main products of reaction, C2, C3 and C4 molecules, oxygenated or not are also detected. The effect of the nature of the catalyst on the relative amounts of these molecules is discussed.

[1] : A. Ozkan, A. Bogaerts, F. Reniers, J. Phys. D: Appl. Phys. 50 (2017) 084004, doi:10.1088/1361-6463/aa562c

9:20am **PS+AS+SE-MoM4 Aluminium Surface Plasma Treatment at Atmosphere Pressure**, ***Lucia Bonova**, I.A. Shchelkanov, C. Ahn, S. Chaudhuri, D.N. Ruzic*, University of Illinois at Urbana-Champaign

Plasma surface treatment at atmosphere pressure is a fast growing industry. Among other applications, surface treatment of metals for adhesion and corrosion resistance improvement has attracted widespread interest. Being operated at atmosphere pressure, various types of plasma discharge devices provide efficient, cheap and large scale processing capabilities. In this area, surface treatment of aluminium for surface properties modification is of great interest as it can decrease steps in process for final coating deposition, reduce usage of harmful chemical reagents, which in their turn require costly dispose procedures, and increase functional coatings performance.

The ECAP experiment (Evaporative Coatings at Atmosphere Pressure) was developed at CPMI (Center for Plasma Materials Interaction at UIUC) as a device and a method for multicomponent metal coatings deposition at atmosphere pressure utilizing a 2.45 GHz microwave plasma torch. The device is capable of coating deposition from a solid metal state and from gas carried precursors as well as composites with processing gas like ZrO. These capabilities make ECAP a very flexible tool for gradient coating deposition for surface functionalization and adhesion improvement. In this gradient coating, the alumina facing materials is gradually replaced with a second layer material with perfect adhesion for final functional coating.

Current work discusses several methods, which were used to improve aluminium surface wettability and adhesion to an epoxy. As a fundamental experiment, we have conducted the simple treatment on aluminium plate by ECAP which operated with feedstock gas of evaporated $H_2O$ and He. It shows remarkable enhanced epoxy adhesion on aluminium sample against the control condition. System configuration for roll-to-roll applications and broad area coatings/cleaning are also discussed.

9:40am **PS+AS+SE-MoM5 The Role of Bulk Liquid Transport Processes in the Plasma-Liquid Interfacial Chemistry**, ***Selma Mededovic Thagard**, M. Vasilev, D. Bohl, P. Conlon*, Clarkson University **INVITED**

Plasmas formed directly in and contacting a liquid are powerful sources of reactive radicals, ions and high-energy electrons and have been successfully used to sterilize water and fruit juices, purify water, synthesize materials and nanoparticles, and for applications in plasma medicine, electrical transmission, and polymer surface treatment. Nevertheless, despite the obvious versatility in processing capabilities, the optimization and broader application of electrical discharge plasmas in and contacting a liquid have been limited due to a general lack of understanding of the underlying physical and chemical processes occurring at the plasma-liquid interface. Despite the significant progress that has been made towards understanding interfacial chemistry of plasmas in the last decade or so (especially for air plasmas contacting water), relative contributions of plasma processes such as formation and diffusion of reactive species and bulk liquid processes such as electrohydrodynamic flow to interfacial dynamics have not been yet determined.

This work investigates the extent to which bulk liquid processes, primarily bulk liquid composition and plasma-induced electrohydrodynamic flow control the rates of chemical reactions at a plasma-liquid interface. We have determined the efficacy of the plasma process for treatment of a wide range of different compounds and used the results of this investigation to construct a model to predict the approximate treatability of any compound based on just a few of the compound's physical properties. Experiments with different initial bulk liquid concentrations of non-surfactant and surfactant compounds have also been performed to investigate how interfacial compound concentration affects its removal rate. Particle Image Velocimetry has been used to quantify the surface velocity of a liquid as a function of its chemical composition.

10:40am **PS+AS+SE-MoM8 Efficiency of Electrolytic Reduction of Aqueous Metal Salts to Metal Nanoparticles at a Plasma-Liquid Interface**, *S. Ghosh, **Ryan Hawtof***, Case Western Reserve University, *P. Rumbach, D.B. Go*, University of Notre Dame, *R. Akolkar, R.M. Sankaran*, Case Western Reserve University

Electrolytic cells with a plasma serving as one or both of the electrodes eliminate the solid metal and allow electrochemical reactions to be carried out at a gas-liquid interface. This is particularly beneficial for the synthesis of metal nanoparticles from metal salts since the deposition of a thin film onto the electrode is avoided. However, because of the complexity of the plasma and the resulting interfacial reactions, the mechanism for metal nanoparticle formation remains unknown.

Here, we designed experiments to understand the mechanism of the reduction of silver nitrate ($AgNO_3$) to silver (Ag) nanoparticles by a previously reported atmospheric-pressure, direct current microplasma operated as the cathode. We applied a well-known methodology in electrodeposition to assess the faradaic efficiency whereby the mass of the synthesized material is compared with the theoretical amount of mass estimated from the charge injected into solution. A faradaic efficiency of 100% would indicate that all the charge is going towards the desired reduction of Ag cations to solid Ag, $Ag^+ + e^-$ --> $Ag^0$, whereas an efficiency less than 100% would suggest that there are side reactions, most probable of which is the second order recombination of (solvated) electrons to form hydrogen gas and hydroxide ions, $e^-_{(aq)} + e^-_{(aq)} + 2H_2O_{(l)}$ --> $H_{2(g)} + 2OH^-_{(aq)}$.

We find that at a relatively high $AgNO_3$ concentration in the bath, the faradaic efficiency depends weakly on the current, reaching values of 100% at 2 mA and decreasing to slightly less than 100% at 6 mA. To corroborate these measurements, the mass change of a Ag foil anode which oxidizes in solution by the reverse of the cathode reaction, $Ag^0$ --> $Ag^+ + e^-$, was compared and found to yield slightly lower efficiencies, but with the same overall trend. At constant current and varying $AgNO_3$ concentration in the bath, the faradaic efficiency was found to drastically decrease to less than 100%. We interpret these results as follows. The kinetics of the primary reactions, $Ag^+$ reduction and second order recombination, depend on the respective rate constants which are similar ($3.7 \times 10^{10}$ M/s and $5.5 \times 10^{9}$ M/s) and the reactant concentrations. At low current or high $AgNO_3$ concentration, the rate of $Ag^+$ reduction is higher than second order recombination and the faradaic efficiency approaches 100%. Conversely, the rate of second order recombination is higher than $Ag^+$ reduction at high current or low $AgNO_3$ concentration, lowering the faradaic efficiency. A reaction model was developed to support these interpretations.

11:20am **PS+AS+SE-MoM10 Amorphous Indium Zinc Oxide (IZO) Semiconductor Films Grown by Atmospheric Plasma-Enhanced Spatial ALD for Application as High-Mobility Channel in Thin Film Transistors**, *A. Illiberi, I. Katsouras, S. Gazibegović, B. Cobb, E. Nekovic,* TNO-Holst Centre, Netherlands, *W. van Boekel, C. Frijters,* TNO-Solliance, Netherlands, *J. Maas,* TNO-Holst Centre, Netherlands, ***Fred Roozeboom***, TNO-Holst Centre & Eindhoven University of Technology, Netherlands, *Y.L.M. Creyghton,* TNO-Solliance, Netherlands, *P. Poodt,* TNO-Holst Centre, Netherlands, *G. Gelinck*, TNO-Holst Centre & Eindhoven University of Technology, Netherlands **INVITED**

Less than a decade ago, InGaZnO has been reported as a new Amorphous Oxide Semiconductor (AOS) channel material replacing conventional amorphous silicon (a-Si:H) for application in thin-film transistor (TFT) circuits in display back panels [1]. Among these, indium zinc oxide (IZO) is emerging as the most promising AOS candidate for next-generation displays based on oxide TFTs because it combines a very high electron mobility with excellent optical transmission and thermal stability [2,3].

We have grown InZnO thin films by plasma-enhanced spatial atomic layer deposition (s-ALD) [4,5] and these layers have been manufactured into oxide TFT and ring oscillator devices which outperform the state-of-the-art. We will describe the growth of InZnO at atmospheric pressure and high deposition rates (~ nm/sec) starting with a short explanation of the basics and the advantages of this novel deposition technique including the use of a special atmospheric plasma source design of the so-called Surface Dielectric Barrier Discharge (SDBD) type [6]. Next, we will show that by varying the ratio of the trimethyl indium and diethyl zinc chemical precursor vapors, the In/(In+Zn) ratio of the film can be accurately tuned over the entire composition range from zinc oxide to indium oxide. TFT test devices with an In/Zn ratio of 2:1 show very high field-effect mobility exceeding 30 $cm^2/V.s$ (Fig. 1), excellent thermal (Fig. 2) and bias stress stability. We will further demonstrate the scalability of the IZO TFTs by fabricating 19-stage ring oscillators operating at 200 kHz which outperform the state-of-the-art.

This superior electrical performance, in combination with the intrinsic advantages of spatial ALD demonstrate the great potential of this atmospheric plasma concept for application in commercial manufacturing of low-cost and large-area AOS-based electronics.

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## Plasma Science and Technology Division
## Room: 23 - Session PS+AS-MoM

## Plasma Processing of Challenging Materials
**Moderators:** Erik V. Johnson, LPICM, Ecole Polytechnique, France, Osamu Sakai, The University of Shiga Prefecture

8:20am **PS+AS-MoM1 Control of Plasma Doping Conformality in FinFET Arrays**, ***Mona Ebrish***, *O. Gluschenkov,* IBM Research Division, *M.J.P. Hopstaken,* IBM T.J. Watson Research Center, *F. Torregrosa*, Ion Beam Services

FinFET devices are rapidly emerging as a standard transistor architecture for extending CMOS scaling beyond the 22 nm technology node because of superior electrostatic channel control. One practical challenge is to achieve a high degree of conformality for source/drain (S/D) extension doping along the Fin sidewalls. Conformal extension doping is crucial to minimize finFET series resistance while maintaining electrostatic channel control. Precise control of transistor characteristics over large-scale CMOS circuits and systems mandates that the extension doping and its conformality be maintained over arrays of finFETs with tight fin pitch. Plasma doping, with its wide distribution of impinging ion angles, provides an alternative to conventional ion beam implantation for fin array sidewalls. The traditional 1D Secondary Ion Mass Spectrometry (SIMS) depth profiling technique is unable to quantify the doping profiles in fin array sidewalls and hence the 1.5D SIMS approach (SIMS through array of fins) is used in this study. The retained sidewall dose measured by 1.5D SIMS is compared to a predicted number of impinging plasma ions that arrive to the fin array with certain angle and energy distributions dependent on the plasma conditions. This comparison takes into account the impinging ion cut off angle caused by adjacent fin shadowing in tight-pitch arrays. Based on those findings, a tuning of the plasma conditions was applied to obtain better than 50% dopant uniformity along the Fin sidewalls. The ability to control impinging ion angle distributions in plasma doping provides a valuable tool for improving doping conformality in tight-pitch fin arrays.

8:40am **PS+AS-MoM2 Study of Plasma-etching Parameter Impacts on Two-dimensional Electron Gas Degradation in AlGaN/GaN Heterostructures**, ***Frédéric Le Roux***, *P. Burtin, N. Posséмé, A. Torres, S. Barnola*, CEA-Leti, France

Formation of the two-dimensional electron gas (2DEG) in AlGaN/GaN heterostructrures is the key-point for successful development of GaN-based power-electronics such as High Electron Mobility Transistors and diodes.

Today, plasma-etching are considered as one of the most critical step in fabrication of such devices. Indeed plasma etching can lead to charge generation (depleting the channel)[1,2], AlGaN amorphisation (modifying the structure and the polarisations of the AlGaN)[3,4] or element implantation inducing charges or traps[5].

In this study, we propose to evaluate the impact of several plasma parameters (chemical, physical and physico-chemical) on 2DEG degradation occurring during silicon nitride etching (selectively to AlGaN). Experiments have been carried out on 200mm wafers using the following stack: 10nm $Si_3N_4$/24nm $Al_{0,22}Ga_{0,78}N$/AlN spacer/2µm GaN/buffer layers. The AlGaN degradation has been determine thanks to Rsheet and Hall measurements.

First the impact of a conventional fluorocarbon etch chemistry ($CF_4/CH_2F_2/O_2$/He) on 2DEG degradation will be presented as an ion-energy function. It will be demonstrated that Rsheet is degraded with the ion energy increase and confirmed by the evolution of career- density and mobility.

Then the pure-chemical etching effects (using wet and downstream-plasma etching process) as well as physical etching effects, with ion bombardment, (using Ion Beam Etching process (IBE)) will be discussed in term of Rsheet.

Finally, the benefit of new silicon nitride etching process, which has already been tested and validated for silicon nitride spacer application[6], has been evaluated for diode contact application. This process is based on two steps. In a first step, the film is modified in volume by a He plasma performed in a conventional etch tool (ICP) followed by a second step of selective removal (HF dip) of the modified layer ($Si_3N_4$) with respect to the non-modified material (AlGaN).

Thanks to this study, the plasma-etching's role in the channel characteristics degradation have been highlighted and linked to the plasma parameter through the Rsheet and Hall measurement evolutions. In order to increase the degradation mechanism understanding engendered by etching steps, physico-chemical characterisations will be developed to determine the degradation sources.

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9:00am **PS+AS-MoM3 Spatiotemporal Non-uniformity of CVD Plasmas and Film Qualities**, ***Masaharu Shiratani***, Kyushu University, Japan **INVITED**

Here we discuss great impact of nanoparticles formed in CVD plasma on uniformity of the plasma and film qualities [1-5]. Uniformity of thickness, composition, structure, and properties is a major concern of plasma CVD films. Multiple precursors including radicals, ions, and nanoparticles contribute to the film formation and hence their flux and flux ratio to the surface determine the film uniformity. Although most studies and text books describe film formation due to radicals and ions, such precursors are predominant only for very low pressure (< 5 Pa); in a pressure range of 10-500 Pa for most plasma CVD, contribution of nanoparticles to the film volume is 10-60% and cannot be disregarded [1-3]. CVD plasma tends to have inherently spatiotemporal non-uniformity of its internal parameters mainly because of nanoparticles. Nanoparticles have long time constant of their nucleation and growth. They tend to be charged negatively and are trapped in plasma. Nanoparticles act as loss sites of electrons, ions, radicals, and nanoparticles; and hence they have great influence on non-uniformity of plasma parameters, deposition rate, and film qualities. Particularly, they tend to give nonlinear response of CVD plasma, such as hysteresis, to discharge power and pressure. We show a model which reproduces well such non-linear response, and contribution of nanoparticles is one of keys to realize uniformity of high quality films [4, 5]. There is plenty of room to improve qualities of plasma CVD films by paying attention to contribution of nanoparticles to the films.

Work partly supported by JSPS KAKENHI grant numbers 26246036 and 16K13922.

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9:40am **PS+AS-MoM5 Surface-driven $CH_4$ generation from $CO_2$ in Low-pressure Non-thermal Plasma**, ***Kazunori Koga***, *S. Toko, S. Tanida, M. Shiratani*, Kyushu University, Japan

The methanation of $CO_2$ attracts attention as the way to produce rocket propellant fuels at Mars because $CO_2$ comprises 95% of the atmosphere of Mars and water exists on Mars [1]. This reaction is called the Sabatier process and has been studied using catalysts under high pressure over 1 atm and high temperature above 200 $^{o}$C to realize a high conversion efficiency. However, the pressure on Mars is 135 times smaller than that of the Earth, and the average temperature is extremely low of -63 $^{o}$C [2]. A method using low-pressure non-thermal plasma allows methanation under low pressure and low temperature conditions [3]. Therefore, the plasma process is suitable for methanation at Mars. Here, we converted $CO_2$ to $CH_4$ using a capacitively coupled plasma (CCP) together with Cu catalyst. Experiments were carried out using a CCP reactor, excited at a frequency of 60 MHz. The electrode diameter was 50 mm and the distance between the electrodes was 6.1 mm. The electrode material was Cu. $CO_2$ gas flow rate was 1.0 sccm and that of $H_2$ was 6.0 sccm . The pressure was 750 Pa and the temperature was room temperature. The discharge power was set in a range of 10 to 100 W. Gas composition in the discharge plasmas was measured with a quadrupole mass spectrometer. $CH_4$ yield depends on surface condition of Cu electrodes, indicating that surface reactions on Cu electrodes dominate the $CH_4$ generation. Moreover, $CH_4$ generation has a long time constant more than 500 s, whereas $CO_2$ conversion has a short time constant of 80 s. These results indicate that $CO_2$ conversion takes place in gas phase by electron impact dissociation, while $CH_4$ generation involves several reaction steps. I will discuss the detail mechanisms at the conference.

Work supported partly by JAXA and JST.

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10:00am **PS+AS-MoM6 Plasma Modification of Carbon Fibres for Tough Carbon Fibre Composites**, ***Sally McArthur***, *R. Radjef, BL. Fox*, Swinburne University of Technology, Australia

Carbon-fibre manufacturing is a well established process that includes a surface treatment and a sizing step which are fast and easily incorporated into the production process. In the electrolytic oxidation steps, ammonium bicarbonate is used to introduce functional and polar groups to the surface while weakly bound basal planes are removed and the surface roughness is increased. All these are desired effects that are then covered with the application of the sizing layer, which protects the fibre surface during subsequent processing steps. The size is generally an epoxy based emulsion that provides handleability, lubrication, protection and is supposed to create a strong bond. This production process creates a complex multilayered interphase that is not well understood. It is believed that the size partially reacts with the surface functional groups, leaving a sizing layer that is depleted in epoxide groups and hence not able to fully cure. Furthermore how do we know that enough hardener diffuses through the matrix to the fibre surface to fully cure the sizing layer in the first place?

The aim of this study is to replace the current surface treatment and sizing step by a two-step plasma approach that allows the formation of a controlled interphase. In part one of this project a comparative study between electrolytic oxidation and air plasma treatment has been performed. In a second stage plasma polymerisation of TMDSO was used to produce films of variable mechanical properties by controlling the plasma power. This talk will focus on the the development and characterisation of the lab-based plasma system used to deposit uniform coatings onto the carbon fibres using a reel-to reel process and dual electrode array.

10:40am **PS+AS-MoM8 Damage Free Plasma Etching Processes of III-V Semiconductors for Microelectronic and Photonic Applications**, ***Erwine Pargon***, *M. Bizouerne, C. Petit-Etienne, L. Vallier, G. Gay, M. Fahed, K. Rovayaz, M. Fouchier, C. Bellegarde, V. Renaud, G. Cunge, O. Joubert*, CNRS-LTM, Université Grenoble Alpes, France, *E. Martinez, N. Rochat*, CEA-Leti, France **INVITED**

Due to their inherent advantages of direct bandgap and high electron mobility, III-V semiconductor materials are today widely used as active materials for a wide range of applications including high-speed and power electronic devices, and many types of opto-electronic and photonic devices. Recent progress in both molecular wafer bonding technology and monolithic heteroepitaxy let envisage the integration of III-V semiconductors directly on a Silicon platform. If successful, such integration paves the way for the emergence of highly performant devices, taking advantages of both III-V unique properties and the maturity of Si processing. Some promising examples are the use of high mobility III–V channel materials to extend the performance of Si CMOS, or the unification of electronics and photonics by combining photonic components with a silicon platform for next-generation optical interconnects. For all these future technologies, development of industrial processes for III-V semiconductors patterning is necessary. Plasma etching allows feature patterning with a nanometric control of the dimension, but one major drawback is the creation of defects in the vicinity of the etched surfaces, that can change the electro-optical properties of the semiconductor, and ultimately compromise the device performance. There is today a lack of knowledge on by which mechanisms and to what extent the plasma etching process induces damage at the III-V pattern sidewalls and the consequence it has on the device performance. The objective of this work is first to provide a better understanding of plasma-induced damage at the sidewalls of micro-nano-patterned III-V semiconductors by establishing a direct link between structural and chemical modifications induced by plasma etching, and opto-electrical properties. Based on such comprehensive know-how, the second objective is to provide technological solutions to minimize this damage in order to propose low damage plasma process compatible with the fabrication of commercial devices. The present study mainly focuses on the plasma etching process development of InGaAs used as a high mobility channel in a FinFET for microelectronic applications and of InGaAs/InP heterostructures used as a laser in hybrid photonic integrated circuits. Etching experiments are carried out in industrial ICP reactors. The structural damage induced at the pattern sidewalls (amorphization, stoichiometry, roughness..) are evaluated by electronic microscopies, AFM and nanoauger spectroscopy. The optical properties of the III-V semiconductors at the pattern sidewalls are analyzed by cathodoluminescence.

11:20am **PS+AS-MoM10 Fabrication of Metal Nanoparticle-dispersed Nanocomposite Films by *In Situ* Plasma Reduction of Metal Cation-containing Polymer Films**, *D.R. Boris*, Naval Research Laboratory, ***Souvik Ghosh***, Case Western Reserve University, *S.C. Hernandez*, Naval Research Laboratory, *C.A. Zorman*, Case Western Reserve University, *S.G. Walton*, Naval Research Laboratory, *R.M. Sankaran*, Case Western Reserve University

Nanocomposites composed of inorganic nanoparticles and polymers have broad applications because of their unique combination of optical, electrical, thermal, and mechanical properties. A key fabrication challenge is dispersion of the two different phases which leads to separation and particle agglomeration. Compared to mixing premade nanoparticles with polymers, *in situ* formation of nanoparticles from a thin film containing the metal precursor and polymer has the potential to improve dispersion. Various approaches to reacting the metal precursor have been explored including heat treatment, UV exposure, and chemical processing. Low-temperature plasmas are particularly unique due to their inherent compatibility with temperature-sensitive polymers, and potential for rapid large-area processing. However, the mechanism for plasma-driven particle formation remains poorly understood.

Here, we carry out a systematic study of *in situ* plasma reduction of metal-cation containing polymer films to form nanoparticle-dispersed nanocomposites. Films were prepared from solutions of silver nitrate ($AgNO_3$) and polyacrylic acid (PAA). Chelation of the polymer with the metal cation produced a precipitate that was collected by centrifugation and cast as a thin film. The films were then exposed to a low-pressure, electron-beam generated plasma operating over a broad set of conditions aimed at delivering a controlled flux of low-energy argon ions. The as-treated films were analyzed with UV-visible absorbance spectroscopy and scanning electron microscopy (SEM). Absorbance confirms the presence of the localized surface plasmon resonance (LSPR) for Ag nanoparticles. The spectra show significant changes in the peak intensities with negligible shifts in the peak wavelength with plasma process changes, indicating that the particle concentration increases or decreases with a relatively constant average particle size. We correlated these changes in particle concentration to the variation in charge fluence at the film surface.

This work is partially supported by the Naval Research Laboratory base program and the National Science Foundation under Grant No. SNM-1246715.

## Scanning Probe Microscopy Focus Topic
## Room: 10 - Session SP+AS+NS+SS-MoM

## New Imaging and Spectroscopy Methodologies
**Moderators:** Wonhee Ko, Oak Ridge National Laboratory, An-Ping Li, Oak Ridge National Laboratory

8:20am **SP+AS+NS+SS-MoM1 Charge Transport through Nanostructures measured with a Multi-Tip STM**, ***Bert Voigtländer***, Forschungszentrum Juelich, Germany **INVITED**

The use of Multi-Tip STM for transport measurements is another step in the recent paradigm shift in scanning probe microscopy transforming from "just imaging" to detailed measurements at the nanoscale. Multi-Tip STM is an ideal technique to study electronic properties, while a current is running through a nanostructure/nanodevice.

We demonstrate how three requirements have to be combined to perform nanoscale charge transport measurements, using the Multi-Tip STM technique: (a) a stable, versatile, and easy to operate Multi-Tip STM instrument, as well as (b) electronics and software, which allow any possible "concerted" Multi-Tip measurements, and last but not least (c) the new method Multi-Tip STM also requires new methodologies for data analysis.

We demonstrate the capabilities of the Multi-Tip STM method to reveal fundamental nanoscale charge transport properties by the following examples: (a) Mapping of resistance profiles and corresponding doping profiles along freestanding GaAs nanowires, (b) measurement of the surface conductivity at semiconductor surfaces, (c) identification of resistivity dipoles in nanoscale potential maps around defects, using scanning tunneling potentiometry, (d) disentangling *in situ* top and bottom conductance of a topological insulator thin film by gate dependent measurements.

9:00am **SP+AS+NS+SS-MoM3 Robust High-Resolution Imaging and Quantitative Force Spectroscopy in Vacuum with Tuned-Oscillator Atomic Force Microscopy**, ***Omur Dagdeviren***, *J. Goetzen,* Yale University, *H. Holscher,* Karlsruhe Institute of Technology (KIT), Germany, *E.I. Altman, U.D. Schwarz,* Yale University

Since the first demonstration of atomic resolution in ultrahigh vacuum more than twenty years ago, frequency modulation-based noncontact atomic force microscopy (FM-NC-AFM) has significantly matured and is now routinely applied to study problems that benefit from high-resolution surface imaging. In FM-NC-AFM, control of the tip's vertical position is accomplished by detecting a shift in the cantilever's resonance frequency upon approach to the sample. Consistently ensuring reliable distance control during extended data acquisition periods has nevertheless remained challenging, as most FM-mode-based control schemes employ three feedback loops that may interfere. As a consequence, sample throughput in FM-NC-AFM is often low compared to ambient condition AFM, where the easy-to-implement amplitude-modulation (AM) control scheme is predominantly used. Transfer of the AM methodology to high-resolution measurements in vacuum is, however, difficult as with AM-AFM, instabilities during approach are common. In addition, the lack of viscous air damping and the related significant increase of the cantilever's quality factor generate prolonged settling times, which cause the system's bandwidth to become impractical for many applications. Here we introduce a greatly simplified approach to NC-AFM imaging and quantitative tip-sample interaction force measurement that prevents instabilities while simultaneously enabling data acquisition with customary scan speeds by externally tuning the oscillator's response characteristics [1]. After discussing background and basic measurement principle, examples for its application to a variety of sample systems are provided [1,2,3,4]. A major advantage of this operational scheme is that it delivers robust position control in both the attractive and repulsive regimes with only one feedback loop, thereby carrying the potential to boost the method's usability.

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9:20am **SP+AS+NS+SS-MoM4 Electrical Transport Measurements with Atomically Precise Probes**, ***Markus Maier***, *J. Koeble, R. Thiel, M. Fenner, A. Pirou, D. Stahl, T. Roth*, Scienta Omicron GmbH

A major challenge in the development of novel devices in nano- and molecular electronics is their interconnection with larger scaled electrical circuits. Local electrical probing by multiple probes with precision on the atomic scale can significantly improve efficiency in analyzing electrical properties of individual structures on the nano-scale without the need of a full electrical integration.

The LT NANOPROBE is a sophisticated instrument that merges the requirements of a 4-probe system, efficiently and precisely navigated by a scanning electron microscope (SEM) and at the same time satisfies the needs for high performance SPM. The excellent stability in the pm range allows for atomic resolution in STM and nc-AFM (QPlus) and expands applications from electrical probing on the nanometer scale towards tunneling and force spectroscopy and the creation of atomically precise structures. The system is operated near thermal equilibrium and temperatures below 5K, specifically also during simultaneous SEM imaging and navigation. The system has been developed towards an extremely low thermal drift in the range of 100pm/h, which is the most important ingredient to allow for enough measurement time on extremely small structures.

We will present measurements that prove the performance level of the instrument, specifically the low thermal drift and stability as well as QPlus AFM measurements, which become important if nanostructures are deposited on an insulating substrate for a better electrical decoupling. We will also show the newest technology improvements, such as high frequency capabilities and optical access for pumped probe experiment. Future technology challenges as well as applications and scientific drivers for this type of scientific instrumentation will be discussed.

9:40am **SP+AS+NS+SS-MoM5 Planar Two-probe Scanning Tunneling Spectroscopy Measurements at the Atomic Level**, ***Marek Kolmer***, Jagiellonian University, Krakow, Poland **INVITED**

We present our recent results obtained on the new Scienta-Omicron low temperature ultra-high vacuum 4-probe STM (LT-Nanoprobe). This unique machine is equipped with 4 STM scanners able to operate on the same surface simultaneously with the stability of the *state-of-art* single tip low temperature STMs [1].

Firstly we show our methodology for fine relative positioning of two STM probes on a surface with unprecedented atomic precision and with a lateral exact probe to probe distance below 50 nm. Secondly we discuss our design of the 2-probe STM experiment, in which both tips are kept in tunnelling conditions above a grounded sample. Then, by applying a DC bias voltage between probes in the described configuration we can detect a probe to probe DC current signal. Moreover, we add a small AC component to a varied DC bias voltage and by demodulation of resulting current signals on each of the probes, we extract corresponding $dI_1/dV_1$ (vertical) and $dI_2/dV_1$ (planar) STS signals. Our method allows a direct testing of the electronic transport properties of atomic-scale structures in a *fully planar* geometry, what is shown on an example of a model system: bare Ge dimer wires on Ge(001) surface. In this case we determine ballistic charge transport regimes in the atomic wires by systematic 2-probe spectroscopic experiments on the probe to probe distances below 50 nm.

Finally, we discuss perspectives for application of the above methodology in characterization of molecular structures, i.e. molecular wires obtained by the on-surface synthesis approach on metal oxide surfaces [2-4].

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10:40am **SP+AS+NS+SS-MoM8 An Ultrafast Scanning Probe Microscopy Technique for Imaging Polarization Switching in Ferroelectric Materials**, ***Suhas Somnath***, *S.V. Kalinin, S. Jesse*, Oak Ridge National Laboratory

Polarization switching in ferroelectric and multiferroic materials underpins the next generation of electronic devices such as tunneling devices, field effect transistors, and race-track memories. The switching mechanisms in these materials are extremely sensitive to local defects and structural imperfections at the micro- and nanometer scale, which have undesirable effects on ferroelectric domains. These considerations led to the development of Piezoresponse Force Microscopy (PFM) for imaging and manipulating local polarization states. In PFM, a micro-cantilever with a conductive tip is brought into contact with the sample surface. Periodic bias applied to the tip deforms the sample, which in turn causes the cantilever to vibrate, and these vibrations are recorded using an optical setup in the microscope. The current state-of-art PFM imaging and spectroscopy techniques measure the bias dependent material deformation either at a single frequency (using a lock-in-amplifier) or over a narrow band of frequencies thereby discarding valuable information from higher vibrational modes of the cantilever and multiple harmonics. As an extension, PFM spectroscopy techniques suffer from serious compromises in the measurement rate, voltage and spatial resolutions since they require the combination of a slow (~ 1 sec) switching signal and a fast (~ 1 – 10 msec) measurement signal. The slow measurement speed results in undesirable compromises between the imaged area, spatial resolution, and voltage resolution.

We report on a new voltage spectroscopy technique applied to PFM that rapidly acquires dense 2D maps of local hysteretic material response. This technique combines the acquisition of the complete information about the cantilever response with intelligent signal filtering techniques to enable direct measurement of material strain in response to the probing bias. Our technique enables precise spectroscopic imaging of the polarization switching phenomena 3,500 times faster than currently reported methods. By rapid acquisition of a large number of hysteretic loops on very dense grids, this technique will enable significant insight into nanoscale polarization dynamics and phenomena such as polarization fatigue or local wall displacements that remain difficult to study at the desired spatial and temporal scales, and are crucial for integration of ferroelectric nanostructures in future electronic devices.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

11:00am **SP+AS+NS+SS-MoM9 Direct Probing of the Graphene-Electrolyte Double Layer Potential**, ***Evgheni Strelcov***, NIST Center for Nanoscale Science and Technology / University of Maryland, *A. Tselev*, University of Aveiro, Portugal, *H.X. Guo, A. Yulaev*, NIST Center for Nanoscale Science and Technology / University of Maryland, *I. Vlassiouk*, Oak Ridge National Laboratory, *N.B. Zhitenev, W. McGehee, B. Hoskins, J.J. McClelland, A. Kolmakov*, NIST Center for Nanoscale Science and Technology

Solid-liquid interfaces play an instrumental role in a broad range of natural phenomena in biological, hydrological, chemical and electrochemical systems. The latter include energy conversion and storage applications, such as fuel cells, supercapacitors, electrochromic devices, and batteries, whose performance strongly depends on the state of the solid-liquid interface. Key elements of this interfacial behavior are the formation of the electrical double layer (EDL), ionic transport through it, ionic adsorption, and Faradaic processes. Thus, understanding the structure and properties of the EDL is of critical importance. Despite more than a century of research on the EDL, its molecular structure and electrode potential dependence remain the subject of frontier research. Only a handful of experimental techniques, including surface force and spectral methods, are currently available for direct probing of the EDL, but even they do not offer adequate spatial resolution.

Here, we report on direct measurement of the EDL potential in a copper (II) sulfate electrolyte with Kelvin Probe Force microscopy (KPFM). The aqueous electrolyte is placed in a multichannel array, consisting of high aspect ratio, 2 μm diameter channels, sealed at the bottom and capped with bilayer graphene at the top. The system can be imaged *in vacuo* with high resolution scanning electron microscopy and KPFM, correlatively. The graphene membrane acts as both an electrode and a seal that prevents the electrolyte from evaporating into the vacuum. The KPFM probe scans over the subnanometer graphene membrane of individual channels and records potential of the EDL formed at the electrified graphene-electrolyte interface. Both graphene and bottom platinum electrode can be biased to modulate the response of the system to polarization. The collected data are compared to numerical simulation of EDL formation.

ES, HG, and AY acknowledge support under the Cooperative Research Agreement between the University of Maryland and the National Institute of Standards and Technology Center for Nanoscale Science and Technology, Award 70NANB14H209, through the University of Maryland. WM and BH acknowledge support of the National Research Council Research Associateship Program.

11:20am **SP+AS+NS+SS-MoM10 Quasiparticle Interference Mapping of ZrSiS**, ***Michael Lodge***, University of Central Florida, *G. Chang, B. Singh*, National University of Singapore, *J. Hellerstedt, M.T. Edmonds*, Monash University, Australia, *D. Kaczorowski*, Polish Academy of Sciences, *M.M. Hosen, M. Neupane*, University of Central Florida, *H. Lin*, National University of Singapore, Singapore, *M. Fuhrer*, Monash University, Australia, *B. Weber*, Nanyang Technological University, Singapore, *M. Ishigami*, University of Central Florida

3D Dirac semimetals are a class of materials whose bulk electronic states are protected by topology, presenting intriguing new systems in which to study the rich physics of the quasiparticles that they host. One such system is the nodal line Dirac semimetal, wherein the conductance and valence bands have a line-like crossing along a closed loop in momentum space and disperse linearly in the vicinity of the resulting line node. This configuration gives rise to the prediction of exotic phenomena such as spin vortex rings, diverging mobility in the limit of vanishing chemical potential, and a linearly increasing dependence of the conductivity on temperature. Many of these compounds have their line node located hundreds of meV above the Fermi level, making direct observation of the line-node inaccessible to experimental techniques such as angle resolved photoemission spectroscopy (ARPES). We employ spectroscopic imaging scanning tunneling microscopy (SI-STM) at 4.5K to visualize the quasiparticle interference with point defects in zirconium silicon sulfide (ZrSiS). In combination with numerical modeling, we identify six groups of quasiparticle scattering vectors allowed within the material, and show that topological protection of the electronic bands is relaxed in the presence of certain defects. We also estimate the location of the line node.

## 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.

(1) Iski *et al.* Electrochimica Acta (**2011**), 56, 1652-1661.

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].

**References**

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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).

## Thin Films Division
## Room: 20 - Session TF+EM-MoM

## ALD for Energy Conversion, Storage, and Electrochemical Processes
**Moderator:** Mark Losego, Georgia Institute of Technology

8:20am **TF+EM-MoM1 Synthesis and Characterization of All Solid-State $SnO_xN_y$/LiPON/Li Batteries**, ***David Stewart****, A.J. Pearse, K. Gregorczyk, G. Rubloff*, University of Maryland, College Park

Atomic layer deposition (ALD) is excellent for depositing conformal thin films on high aspect ratio substrates, and due to the good thickness control and uniformity, ALD allows us to push the limits of thin film batteries. To produce solid-state lithium ion batteries on such substrates new processes for anodes, high-capacity cathodes, and solid-electrolytes must continue to be developed and characterized. Sn and $SnO_2$ have been well studied as alloy/conversion electrodes in the literature, while the properties of $Sn_3N_4$ and $SnO_xN_y$ have yet to be explored in any detail. To study the differences in the electrochemical performance of $SnO_2$, $Sn_3N_4$, and $SnO_xN_y$, an ALD process was developed that allows for highly tunable N/O ratios. In this study tetrakis(dimethylamido)tin (TDMA(Sn)) was used as the metal-organic precursor in combination with remote nitrogen plasma ($^p$N) and $H_2O$ was used to introduce oxygen content. For the pure nitride phase, a broad temperature window was found between 150-250 °C, over which the growth rate per cycle (GPC) was ~ 0.55 Å. While only very short pulse times (< 1 s) were required for saturation of the TDMA(Sn), relatively long $^p$N exposures (> 20 s) were required for GPC saturation. We then showed that by varying $H_2O$ super cycles the relative concentration of O and N in the film can be controlled between 0% N and 95% N.

To study the electrochemical performance of these materials solid-state half-cells were constructed using $SnO_2$, $Sn_3N_4$, and $SnO_xN_y$ thin films versus thermally evaporated Li. A 100 nm thin film of LiPON was deposited as the solid electrolyte by thermal ALD [1]. This electrolyte layer is thick enough to provide good electrical insulation and thin enough to allow fast ionic diffusion, however when cycled to voltages below 0.4 V vs $Li/Li^+$ the half-cells shorted, possibly due to mechanical breakdown of the LiPON layer from significant volume expansion of the anodes during the alloying reaction with Li. The $Li_2O$ matrix formed from $SnO_2$ is expected to be more stable, but with lower ionic conductivity than the $Li_3N$ matrix formed from $Sn_3N_4$. Galvanostatic intermittent titration and electrochemical impedance spectroscopy were used to analyze the ionic conductivity of the anodes before and after the initial conversion reaction and as a function of N/O ratio. The high capacity of the $SnO_xN_y$ electrodes in combination with the excellent ionic conductivity and mechanical properties of the ALD LiPON makes these films attractive for applications in 3D Li-ion batteries.

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8:40am **TF+EM-MoM2 Molecular Layer Deposition for Applications in Lithium-Ion Batteries**, *K. Van de Kerckhove, F. Mattelaer, J. Dendooven,* ***Christophe Detavernier***, Ghent University, Belgium

Molecular layer deposition (MLD) of hybrid organic-inorganic thin films called *titanicones*, *vanadicones*, *tincones*, and *alucones* was investigated for electrode and solid electrolyte applications in lithium-ion batteries.

The titanicone, vanadicone and tincone films were studied as electrode materials, both as anodes and cathodes. Novel MLD processes were developed for these materials and were based on an alkylamine metal precursor (TDMAT, TEMAV, TDMASn) and glycerol (GL) as the organic reactant [1,2]. Linear and self-limited growth could be achieved for these metalcones in a broad temperature range with temperature-dependant growth rates ranging from 0.2 to 1.3 Å/cycle. Film growth was studied in situ with spectroscopic ellipsometry (SE) and infrared spectroscopy (FTIR). The as-deposited films appeared to be electrochemically inactive in all cases. A post-deposition heat treatment up to 500°C in either inert (helium) or oxidizing (air) atmosphere was able to electrochemically activate the films. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements showed that all carbon was removed during calcination in air and that the films crystallized. However, annealing in inert atmosphere conserved the carbon content of the film and thus the films remained amorphous. The performance with increasing charging and discharging rate, and cyclability of the heat-treated MLD electrodes was tested against their respective metal oxide references. The He-annealed metalcones emerged from these tests as the best performing electrodes at higher rates and with improved capacity retention and stability during repeated charging and discharging.

The transformation of alucone films, deposited with the TMA and ethylene glycol (EG) or GL process, into porous aluminium oxide was examined. Porous, non-conducting materials are interesting for lithium-ion battery research since they may serve as the matrix template for solid composite electrolytes. Calcination in air and water etching proved to be the most successful methods. For the calcination treatment, a clear relation was found between the ramp rate during both heating and cooling and the resulting porosity of the film. The aging behaviour of the films in ambient atmosphere was also investigated with FTIR and showed that the films deposited with EG decompose in a matter of only a few hours, as opposed to those deposited with GL.

[1] Van de Kerckhove et al., ***Dalton Trans.***, 2016,**45**, 1176-1184.

[2] Van de Kerckhove et al., ***Dalton Trans.***, 2017,**46**, 4542-4553.

### 9:00am **TF+EM-MoM3 Engineering Hybrid Thin Film Electrolytes for 3D Lithium-ion Battery Applications**, ***Ryan Sheil***, *J. Lau,* University of California at Los Angeles, *P. Moni,* MIT, *C. Choi,* University of California at Los Angeles, *K. Jungjohann,* Sandia National Laboratories, *J. Yoo,* Los Alamos National Laboratory, *K. Gleason,* MIT, *B. Dunn, J.P. Chang,* University of California at Los Angeles

3D battery architectures have the potential to meet the power and energy density demands of next generation microelectronic devices. One requirement in the utilization of 3D based electrodes is the incorporation of a solid electrolyte that can be coated pinhole free and conformally on high aspect ratio structures. Lithium aluminosilicate ($Li_xAl_ySi_zO$, LASO), a solid oxide Li-ion conductor, synthesized by atomic layer deposition (ALD) is a promising electrolyte material for 3D battery applications due to its adequate ionic conductivity ($8.2\times10^{-8}$ S/cm) in thin film applications as well as its ability to improve electrode stability. The self-limiting nature of ALD allows precise thickness and composition control when applied to complex metal oxides. Lithium tert-butoxide (LTB), trimethylaluminum (TMA), and tris(tert-butoxy)silanol (TTBS), were precursors used to synthesize LASO by ALD.

In order to further explore potential material properties, ALD deposited LASO was combined with a polymer electrolyte, poly-(tetravinyltetramethylcyclotetrasiloxane) (PV4D4) deposited via initiated chemical vapor deposition (iCVD). The LASO solid electrolyte offers high electrical resistance and chemical stability at the electrochemically active interface, while the pV4D4 solid electrolyte offers improvements in the mechanical integrity of the electrode. A hybrid film consisting of 5 nm LASO and 400 nm PV4D4 demonstrated a room temperature ionic conductivity of $3.4 \times 10^{-7}$ S/cm, showing no significant increase in interfacial resistance. Integration with both 2D and 3D electrodes has shown substantial improvements in cycling and increased coulombic efficiency.

Current research on Li-ion batteries is directed at creating next generation electrode materials. One of the most viable 3D designs is through the use of nanowire electrodes, in which Si and Ge can offer much larger charge capacities (8444 A h $L^{-1}$ for $Li_{15}Si_4$ and 7366 A h $L^{-1}$ for $Li_{15}Ge_4$, respectively) than traditional carbon based anode materials, but suffer large volume expansion upon lithiation. Using an in-situ TEM electrochemical characterization technique, dynamic processes and structural changes are able to be observed during the lithiation/delithiation of a SiGe nanobattery in real time. Preliminary results show that ALD $Li_xAl_ySi_zO$-coated $Si_{0.4}Ge_{0.6}$ alloy nanowire demonstrates lithiation and delithiation with an intact solid state electrolyte layer with ~39% radial expansion observed upon lithiation.

### 9:20am **TF+EM-MoM4 Carbon Encapsulated CNT Micropillars for Silicon Lithium Ion Battery Electrodes**, ***Kevin Laughlin***, *E. Laughlin, R. Fan, R.F. Davis, R.R. Vanfleet, J. Harb,* Brigham Young University

Here we present work on a hierarchical approach to structuring and encapsulating carbon nanotube (CNT) based carbon monoliths. Prior work has shown silicon has high gravimetric capacity, but increases by ~300%, and forms an unstable solid electrolyte interphase (SEI). High stability and lifetime operation requires nanostructuring of the silicon to alleviate stresses caused by the large expansion of the silicon upon Li alloying, and an encapsulation layer to restrict SEI build up. These CNT structures provide: porous scaffolding for silicon to expand to manage stress on multiple scales, a long conductive path for lithium transfer resulting in tall electrodes, and protection from unstable SEI formation. At high silicon loadings even nanoscale layers of silicon result in stresses large enough to cause mechanical damage to the electrode and encapsulation layer, resulting in lower capacity and cell lifetimes. By patterning the CNT scaffolding, we can contain the stresses caused by lithiation.

### 9:40am **TF+EM-MoM5 Porous Oxide Shell on the Supported Gold Nanoparticles Synthesized via Polymer-Templated Atomic Layer Deposition**, ***Haoming Yan***, *X.Z. Yu, Q. Peng,* University of Alabama

Ultra small (≤ 5 nm) metal nanoparticles (USMNPs), especially Au, have attracted increasing attention due to their remarkable catalytic activity and selectivity in many important reactions. However, their catalytic properties are greatly affected by the poor thermal stability and the macro-molecular capping ligand (MCL) layer on their surfaces. Encapsulating the USMNPs with a porous oxide shell (pOXIDE) is a solution for both issues. So far, there has been limited success in generating the pOXIDE shell on the supported USMNP without significantly blocking its active sites. The objective of this work is to demonstrate the MCL layer templated atomic layer deposition (ALD) can be applied to synthesize the pOXIDE shell on the USMNPs to improve their thermal stability while keeping most of the surface active sites on USMNPs for the catalytic reaction.

### 10:00am **TF+EM-MoM6 Three-Dimensional Solid State Batteries Grown Via Atomic Layer Deposition**, ***Alexander Pearse***, *T. Schmitt, D. Stewart, E. Sahadeo, K. Gregorczyk,* University of Maryland, College Park, *K. Gerasopoulos,* Johns Hopkins Applied Physics Lab, *G. Rubloff,* University of Maryland, College Park

Thin film solid state batteries have multiple attractive properties, including low interfacial impedance, exceptional cycling stability, and intrinsic safety, but have not seen significant implementation because their overall capacity is very low (on the order of 0.1 mAh/$cm^2$). This is a consequence of their growth by physical vapor deposition, which limits them to planar substrates. In this configuration, increasing areal capacity necessarily sacrifices rate performance due to slower ionic diffusion in thicker electrodes. Realizing practical energy or power densities in thin film SSBs will involve the development of entirely new fabrication processes in order to allow the integration of thin film SSBs with 3D substrates, such as micromachined silicon or conductive fabrics. In particular, 3D designs allow the decoupling of capacity and rate performance for area-normalized metrics.

We describe the development and synthesis of a solid state lithium-ion battery film stack grown entirely by atomic layer deposition (ALD), which allows us to successfully integrate solid state energy storage with 3D structures. The entire device is fabricated at temperatures at or below 250C, allowing for compatibility with a broad variety of substrates and processing environments. We utilize a simple electrochemical process for inserting free lithium ions into a crystalline cathode, avoiding the need to integrate lithiation into the ALD growth process itself. The solid electrolyte is a lithium polyphosphazene compound (a variant of LiPON) grown by a 2-precursor thermal process (Pearse et al. Chemistry of Materials 2017). The battery itself is comprised of a $LiV_2O_5$ – $Sn_xN_y$ couple, providing a reversible capacity of approximately 35 μAh/$cm_2$ $\mu m_{LVO}$ with an average discharge voltage of 2V. By growing these batteries into micromachined silicon structures with aspect ratios of up to 10, we are able to increase areal capacity by nearly one order of magnitude while simultaneously improving capacity retention at high rates- a type of scaling not possible for planar devices. We also discuss challenges associated with interface chemistry in the ALD growth environment and with patterning highly conformal films, and compare device performance to finite element electrochemical simulation.

### 10:40am **TF+EM-MoM8 Systematic Investigation of Geometric Effects in Porous Electrodes for Energy Conversion Reactions**, ***Julien Bachmann***, University of Erlangen, Germany **INVITED**

Inexpensive energy conversion devices necessitate novel strategies towards reducing the need for rare functional materials. One such strategy consists in accurately controlling the interface's geometry.

In our work, the pore walls of an anodic nanoporous template are coated with either galvanic deposition or atomic layer deposition (ALD) to obtain structured electrode surfaces that provide the experimentalist with a well-defined, tunable geometry. Indeed, the platform consists of a hexagonally ordered array of metallic or oxidic nanotubes of cylindrical shape, embedded in an inert matrix. The diameter of the tubes can be defined between 20 and 300 nm and their length between 0.5 and 100 μm, approximately. They can be utilized as a model system in which the electrode's specific surface area can be increased and its effect on the electrocatalytic current characterized systematically.

Diffusion-limited electrochemical transformations remain unaffected by changes in the length of the electrode's pores, whereas the steady-state galvanic current density observed for slow multielectron transformations increases linearly with the pore length. In particular, this approach enables us to achieve an increase of the electrochemical water oxidation turnover at neutral pH on iron oxide surfaces by three orders of magnitude. These results highlight a strategy for optimizing electrochemical energy transformation devices which could be generalized: the geometric tuning of catalytically mediocre but abundant and cost-effective material systems.

11:20am **TF+EM-MoM10 Development of a Reduction-resistant Oxide Electrode for Dynamic Random Access Memory Capacitor**, ***CheolJin Cho****, M.-S. Noh, W.C. Lee*, Korea Institute of Science and Technology, Republic of Korea, *C.H. An*, Seoul National University, Republic of Korea, *C.-Y. Kang*, Korea Institute of Science and Technology, Republic of Korea, *C.S. Hwang*, Seoul National University, Republic of Korea, *S.K. Kim*, Korea Institute of Science and Technology, Republic of Korea

Rutile phase $TiO_2/RuO_2$ structures have attracted great interests as a new material system for next-generation dynamic random access memories (DRAM) capacitors because of the high dielectric constant (> 80) of the rutile $TiO_2$. A conducting oxide electrode, $RuO_2$, enables the $TiO_2$ dielectric to be crystallized into a rutile phase at low temperatures (< 300 ºC). Since $RuO_2$ has a high work function, it is effective to suppress leakage current by Schottky emission which is a main conduction mechanism of $TiO_2/RuO_2$. However, the $RuO_2$ electrode is easily reduced during the post-annealing under forming gas atmosphere for trap passivation at the gate oxide/Si interface. Subsequently, the dissociated oxygen ions from $RuO_2$ cause problems such as the oxidation of W plug. The oxidation of W plug causes a fatal deterioration in device operation because the W plug acts as a path through which the charges of the capacitor move. Also, physical damage such as cracks will also occur when $RuO_2$(rutile) is reduced to Ru(hexagonal close-packed, HCP). For these reasons, we suggest a $SnO_2$-based electrode, which is a reduction-resistant material, as a new oxide electrode for DRAM capacitors. The reduction reaction of $SnO_2$ is thermodynamically more difficult than that of $RuO_2$. Also, a small amount of Ta ions is incorporated into the $SnO_2$ films to enhance the conductivity of the electrode. The resistivity of $SnO_2$ is reported to reach down to $10^{-4}\Omega\cdot$cm by Ta doping, which is sufficient for use as an electrode of DRAM capacitor. Furthermore, the Ta-doped $SnO_2$ films are well crystallized into a rutile phase, thereby leading to the formation of rutile $TiO_2$ at a low growth temperature (< 270 ºC). Therefore, we demonstrate that Ta-doped $SnO_2$ would be a promising candidate for the electrodes for next-generation DRAM capacitors.

## Tandem MS Focus Topic
## Room: 5 & 6 - Session TM+AS-MoM

### New Instrumentation Featuring Tandem MS

**Moderators:** Chris Anderton, Pacific Northwest National Laboratory, Daniel Graham, University of Washington

8:20am **TM+AS-MoM1 *In Situ* MS/MS Analysis on Biological Samples using Imaging Secondary Ion Mass Spectrometry (SIMS)**, ***Hua Tian***, Pennsylvania State University **INVITED**

SIMS imaging allows characterization of biomaterials with high lateral resolution. The method has not, however, yet gained popularity within the biological community. One reason is the need for MS/MS analysis due to isobaric interferences associated with the complex composition of biomaterials. Although MS/MS has been routine in imaging mass spectrometry (IMS) with matrix assisted laser desorption ionization (MALDI), it is rarely incorporated with SIMS imaging. Until recently, only a few SIMS instruments had the capability of tandem or parallel MS/MS imaging, for example the J105 3D Chemical Imager, PHI nanoTOF II and IonToF Orbitrap Hybrid [1-3]. The identification of lipids and metabolites in various biosystems, such as Drosophila brain section[4], Zebra Finch brain section, Zebrafish whole body section[1] and bacteria [2], has been reported so far. The precise precursor selection, high lateral resolution and high energy collisional fragmentation are the must-have for the design of new instrumentation for MS/MS capability. Gas cluster ion source (GCIB) is also a necessity for generating sufficient precursor ions especially at extended mass range of SIMS spectra, allowing for a much greater variety of biomolecule studies. Here, we present a review of the current state of MS/MS in SIMS, and illustrate the power of this technique using a hybrid mass spectrometer that employs shaped field bunching for injection into the collision cell. The possibility to utilize laser-induced photo-fragmentation in this instrument is also discussed.

1. Fisher, G. L.; Bruinen, A. L.; Ogrinc Potočnik, N.; Hammond, J. S.; Bryan, S. R.; Larson, P. E.; Heeren, R. M. A., A New Method and Mass Spectrometer Design for TOF-SIMS Parallel Imaging MS/MS. *Analytical Chemistry* **2016,***88* (12), 6433-6440.

2. Wehrli, P. M.; Lindberg, E.; Angerer, T. B.; Wold, A. E.; Gottfries, J.; Fletcher, J. S., Maximising the potential for bacterial phenotyping using time-of-flight secondary ion mass spectrometry with multivariate analysis and Tandem Mass Spectrometry. *Surf Interface Anal* **2014,***46*, 173-176.

3. Hybrid SIMS. https://www.iontof.com/hybrid-sims-ms-ms-organic-mass-spectrometry-surface-analysis.html (accessed April 28, 2017).

4. Phan, N. T. N.; Munem, M.; Ewing, A. G.; Fletcher, J. S., MS/MS analysis and imaging of lipids across Drosophila brain using secondary ion mass spectrometry. *Analytical and Bioanalytical Chemistry* **2017**, 1-10.

9:00am **TM+AS-MoM3 Molecular Depth Profiling with a New Hybrid SIMS Instrument for Improved Molecular Identification using Tandem MS**, ***Alexander Pirkl****, R. Moellers, H.F. Arlinghaus, J. Zakel, D. Rading, E. Niehuis*, ION-TOF GmbH, Germany

The characterisation of organic layer systems is of increasing interest in many research areas. Since the application of large argon clusters as sputter species in SIMS, depth profiling of almost all organic materials has become feasible whilst retaining the intact molecular information during the profile.

However, molecular identification of unknown substances, e.g. contaminants, can be hampered by constraints in mass resolution and mass accuracy of a standard TOF analyser. To overcome this problem, we have developed a new Hybrid SIMS instrument, which uniquely combines all advantages of a state-of-the-art TOF-SIMS with the mass spectrometry performance of an Orbitrap mass analyzer (Q Exactive$^{TM}$ HF) [1]. The Q Exactive mass spectrometer provides a mass resolution of more than 240,000 @ m/z = 200, sub ppm mass accuracy, and fully integrated MS/MS capabilities that allow low energy collision induced fragmentation for structural analysis of complex molecules. All in all this dramatically increases the level of confidence for the SIMS analysis.

In this contribution, we will present the new instrument and discuss applications from various fields including organic electronics. We will demonstrate how the extremely high mass resolution of the Q Exactive mass spectrometer can be advantageously used to resolve mass interferences which cannot be separated in a standard TOF-SIMS instrument. We will also show examples of structural analysis using the high-performance MS/MS capabilities and discuss the new possibilities of the unique TOF / Q Exactive mass spectrometer combination.

[1] Passarelli et al, The 3D OrbiSIMS – A new Method for Label-Free Metabolic Imaging with Sub-cellular Lateral Resolution and High Mass Resolution, submitted 2017.

9:20am **TM+AS-MoM4 Spatially-resolved Tandem Mass Spectrometry Increases Molecular Confidence in a Multimodal Mass Spectrometry Imaging Investigation of a Tripartite Plant-fungus-cyanobacteria Interaction**, ***Dušan Veličković***, Pacific Northwest National Laboratory, *A.A. Carrell*, Duke University, *R.K. Chu*, Pacific Northwest National Laboratory, *D. Pelletier*, Oak Ridge National Laboratory, *L. Paša-Tolić*, Pacific Northwest National Laboratory, *D.J. Weston*, Oak Ridge National Laboratory, *C.R. Anderton*, Pacific Northwest National Laboratory

Plant microbiomes represent a complex mix of interacting species with diverse physiologies and phylogenetic origins. Their functional outcomes are critical to biogeochemical cycles, yet measuring molecular (e.g., metabolite) exchange among interacting species is a major technical challenge. Traditional bulk metabolomic technologies are often limited in their ability to distinguish between molecules that remain localized within microbes and exuded molecules that are in proximity, thus often disregarding the multifaceted chemical exchange within and between interacting species. Mass spectrometry imaging (MSI) methodologies have been recently adopted to visualize the flow of metabolites produced by agar-supported microbial colonies. Several ionization modalities are suitable for MSI of microbial communities, with matrix-assisted laser desorption/ionization (MALDI) being most commonly used. When coupled with ultra-high resolution mass analyzers (e.g., Fourier transform ion cyclotron resonance mass spectrometers; FTICR-MS), these imaging sources offer the high mass resolution and accuracy needed for putative identification of metabolites in individual pixels in the image. However, orthogonal methodologies (e.g., tandem MS) are often required for confident metabolite identification.

Herein, we explored the interactions within a tripartite system of moss, cyanobacteria, and fungus using a multimodal imaging strategy, which employs liquid extraction surface analysis (LESA) tandem MSI to examine previously MALDI imaged samples. This method improved exometabolite identification confidence by preserving spatial dimensionality in the tandem MS experiment. Specifically, we found the combination of these two imaging modalities generated very congruent mass spectral information, providing the link between highly accurate structural information offered by LESA and high spatial resolution attainable by MALDI. Finally, FTICR-based secondary ion mass spectrometry provided new insights into tripartite community using correlative fragment data (SIMS and LESA-MS/MS), while delivering higher lateral resolution MS images. These multimodal imaging results offer detail metabolic insights into a moss, cyanobacterium, and fungus in isolation and when in a tripartite symbiosis.

9:40am **TM+AS-MoM5 The Biosynthesis of Protective Metabolites in Amazonian *Sextonia rubra* Revealed by 100 nm-Scale TOF-SIMS Tandem MS Imaging**, ***Gregory L. Fisher***, Physical Electronics, *T. Fu, D. Touboul*, Institut de Chimie des Substances Naturelles, CNRS, France, *S. Della-Negra*, Institut de Physique Nucléaire, CNRS, France, *E. Houël, N. Amusant, C. Duplais*, Cirad, UMR EcoFoG, AgroParisTech, CNRS, INRA, France, *A. Brunelle*, Institut de Chimie des Substances Naturelles, CNRS, France

We have explored the botanical synthesis of bioactive molecules in the wood of *S. rubra* (Figure 1) via TOF-SIMS Parallel Imaging MS/MS. This investigation is part of an effort to develop a new strategy for investigating natural product formation in relation to the secondary metabolite synthesis during heartwood formation. The TOF-TOF tandem mass spectrometer of the PHI *nanoTOF* II enabled, for the first time in this field of study, simultaneous surface screening of the botanical matrix chemistry by TOF-SIMS ($MS^1$) imaging and targeted identification of biosynthetic components by MS/MS ($MS^2$) imaging [1]. Imaging of molecules with unambiguous identification occurred in minutes without observable degradation of the specimen. Hence, the wood chemistry was broadly profiled while multiple tandem MS imaging analyses were performed for discovery.

The metabolites of rubrynolide and rubrenolide, having significant xylophage toxicity and antifungal properties [2], are produced in oil cells that are found in close proximity to both vessels and parenchyma cells. Moreover, there are thought to be several bio-molecular precursors en route to these bioactive metabolites. Our goal was to identify biosynthetic precursors, and to verify their coincidence with rubrynolide and rubrenolide, via tandem MS imaging. We were able to demonstrate the presence of numerous precursors and to confirm or derive their structure using the tandem MS product ion spectrum, thus contributing in the exploration of natural product biosynthesis.

[1] (a) G.L. Fisher, A.L. Bruinen, N. Ogrinc Potočnik, J.S. Hammond, S.R. Bryan, P.E. Larson, R.M.A. Heeren, *Anal. Chem.* **2016**, DOI: 10.1021/acs.analchem.6b01022. (b) G.L. Fisher, J.S. Hammond, P.E. Larson, S.R. Bryan, R.M.A. Heeren in *SIMS XX Proceedings* (Ed.: D. Castner), Wiley, New Jersey, **2016**, DOI: 10.1116/1.4943568.

[2] (a) A.M.S. Rodriguez, P.N.E.T. Theodoro, V. Eparvier, C. Basset, M.R.R. Silva, J. Beauchêne, L.S. Espíndola, D. Stein, *J. Nat. Prod*. **2011**, DOI: 10.1021/np1001412. (b) A.M.S. Rodriguez, N. Amusant, J. Beauchêne, V. Eparvier, N. Lemenager, C. Baudasse, L.S. Espíndola, D. Stein, *Pest Manag. Sci*. **2011**, DOI: 10.1002/ps2167.

10:40am **TM+AS-MoM8 Metabolite Annotation for Ultra-HR Imaging Mass Spectrometry: MS1 and Beyond**, ***Theodore Alexandrov***, European Molecular Biology Laboratory, Germany **INVITED**

Metabolite imaging mass spectrometry promises to localize small molecules, metabolites, and lipids in tissues, microbial and cell cultures, and to interpret them in the context of cellular heterogeneity. However, just until recently the molecular interpretation of the big data generated by this technique was hampered by the lack of bioinformatics for metabolite identification. We recently developed and implemented a bioinformatics approach that allowed us to identify hundreds of metabolites from hundreds of datasets from various biological systems. We will present how this big data mining approach helps extract molecular knowledge from terabytes of imaging mass spectrometry data, find the link between metabolism and disease, and picture metabolites across hundreds of datasets.

11:20am **TM+AS-MoM10 Multivariate Analysis of combined ToF-SIMS and Orbitrap-SIMS data**, ***Henrik Arlinghaus***, *M.R. Keenan, A. Pirkl, R. Moellers, E. Niehuis*, ION-TOF GmbH, Germany

Advances in SIMS instrumentation, such as the advent of gas cluster ion sources, have greatly increased the analysis capabilities on organic samples, e.g. by reducing molecular fragmentation. However, the identification of molecules may still be limited by the mass resolution and mass accuracy of the analyzer. A Hybrid SIMS instrument[1], combining a ToF-SIMS mass analyzer and an Orbitrap$^{TM}$ mass analyzer (Q Exactive$^{TM}$ HF) has been developed in order to overcome these limitations, combining the high lateral and depth resolution and repetition rate of the ToF-SIMS analyzer with the high mass resolution, mass accuracy, and MS-MS capabilities of the Q Exactive HF analyzer (240,000 @ m/z = 200, sub ppm accuracy). This instrument generates a vast amount of data, rendering manual analysis of the full dataset impractical.

Multivariate analysis (MVA) may be used to reduce complex datasets to a small set of relevant factors, simplifying data interpretation. Established multivariate techniques, such as principal component analysis (PCA), have been used to analyze everything from a small set of inorganic spectra to complex three dimensional organic samples consisting of hundreds of millions of voxel spectra, such as OLEDs. These techniques are now routinely used for ToF-SIMS data analysis in many laboratories.

We will present results of multivariate analysis of datasets acquired using a Hybrid SIMS instrument, where we simultaneously analyzed both the ToF-SIMS and Orbitrap-SIMS data. This type of analysis presents unique challenges, such as contending with vastly different detector technologies and the corresponding differences in noise characteristics.

[1] Passarelli et al, The 3D OrbiSIMS – A new Method for Label-Free Metabolic Imaging with Sub-cellular Lateral Resolution and High Mass Resolution, submitted 2017.

## Vacuum Technology Division
## Room: 7 & 8 - Session VT+MN-MoM

### Progress with Measurement in Vacuum
**Moderators:** Martin Wüest, INFICON Ltd., Liechtenstein, Steve Borichevsky, Applied Materials, Varian Semiconductor Equipment

8:20am **VT+MN-MoM1 New Vacuum Standard by Ultra-Precise Refractive Index Measurement**, ***Jay Hendricks***, *J.E. Ricker, J.A. Stone, P. Egan, G.E. Scace, K.O. Douglass, D.A. Olson, G.F. Strouse*, NIST

NIST has now completed the 5th year of an Innovations in Measurement Science (IMS) initiative with the aim of developing a new paradigm in the methodology of pressure and vacuum measurement and primary standards. The research program has now successfully developed a new standard that is based on the ultra-precise measurement of gas refractive index. This advance now enables NIST to replace mercury manometer standards with a new quantum-based, photonic technique. The new standard, is based on the fundamental physics of light interacting with a gas, and when the gas is helium, the refractive index is based upon first principle quantum chemistry calculations and is realized as a primary standard. For the vacuum community, a photonic realization of the pascal represents a fundamental change in how the unit of pressure is realized in that it will be directly related to the density of a gas by the temperature, refractive index, and Boltzmann constant. The photonic technique has now achieved important benchmarks in performance when compared to the existing primary standards based on mercury manometers: The photonic technique has a 20x smaller footprint, 100x faster sensing response time, extended to 100x lower pressure, a tenth of a mPa resolution over the full range, and has demonstrated impressive accuracy, reproducibility and hysteresis for an emerging technique [1]. Data will be presented that shows this technique has now reached or surpassed mercury manometer performance which creates a new paradigm for vacuum metrology and realization of the SI unit, the pascal. Future NIST work will explore improvements that will enable the device to become a portable pressure and vacuum standard for international key comparisons in pressure and vacuum metrology.

[1] Comparison measurements of low-pressure between a laser refractometer and ultrasonic manometer, Review of Scientific Instruments, Volume 87, May 2016

Accepted: May 2016, Issue 5, 10.1063/1.4949504

8:40am **VT+MN-MoM2 Construction and Testing of the NIST Variable Length Optical Cavity Pressure Standard**, ***Jacob Ricker***, *J. Hendricks, G.E. Scace, P. Egan, J.A. Stone*, NIST

NIST is constructing and testing a new refractometer, referred to as the Variable length optical cavity (VLOC), that will redefine how pressure and vacuum is measured. NIST has shown in previous talks and papers that this technique will replace all mercury manometers in the near future. However, the critical final piece of this project is to base the traceability of pressure measurements to fundamental constants of the universe and not on the physical artifacts like mercury density in a manometer. Theoretical quantum mechanics have been used to precisely calculate the refractivity (n-1) of a gas. NIST will experimentally verify these calculations and provide experimental measurements of refractivity for other gasses/mixtures.

The engineering of the VLOC will be discussed along with limitations and technical complications that have arisen. Specifically, the distortions of the optical cavities and methods to overcome these limitations. Additionally, the steps required to maintain ultra-high purity gas will be discussed. Finally, the testing and final steps to achieve full operation will be discussed and the relation to the 2018 redefinition of the Boltzmann constant.

9:00am **VT+MN-MoM3 Fast-Switching Dual Fabry-Perot Cavity-based Optical Refractometry – A Powerful Technique for Drift-Free Assessment of Gas Refractivity and Density**, ***Ove Axner***, *I. Silander*, *T. Hausmaninger*, Umeå University, Sweden, *M. Zelan*, RISE Research Institutes of Sweden, Sweden **INVITED**

Since pressure has a temperature dependence it is not trivial to accurately assess gas amounts by pressuring measuring devices. However, the (number) density does not suffer from such limitations. Optical Refractometry (OR) is a powerful technique for assessment of gas refractivity and density. The highest resolution is obtained when performed in a Fabry-Perot (FP) cavity. In FP-Cavity based OR (FPC-OR) the change in the frequency of laser light, locked to a longitudinal mode of a FP cavity, is monitored while the amount of gas in the cavity is being changed. Since frequency is an entity that can be assessed with enormous precision, the precision of FPC-OR can be extremely high. However, although potentially very powerful, FPC-OR is often limited by thermal deformation of the spacer between the mirrors. A partial remedy to this is to use two FP cavities, termed Dual FPC-OR (DFPC-OR).

We have prophesied that if measurements could be done under drift free conditions, the technique would be able to circumvent most of these limitations. A possible strategy for drift-free DFPC-OR, termed fast switching DFPC-OR (FS-DFPC-OR), is presented in which measurements are made under such short times that the drifts of the cavity can be disregarded. The methodologies developed circumvent the problem with volumetric expansion, i.e. that the gas density decreases when gas is let into the measurement cavity by performing a pair of measurements in rapid succession; the first one assesses the density of the gas transferred into the measurement cavity by the gas equilibration process, while the second automatically calibrates the system with respect to the ratio of the volumes of the measurement cavity and the external compartment. The methodologies for assessments of leak rates comprise triple cavity evacuation assessments, comprising two measurements performed in rapid succession, supplemented by a third measurement a given time thereafter.

We predict that refractivity and density can be assessed, under STP conditions, with a precision in the $10^{-9}$ range. The absolute accuracy is expected to be given by the calibration source. If characterized with respect to an internal standard, the accuracy can be several orders of magnitude better. The temperature dependence of FS-DFCB-OR is exceptionally small, typically in the $10^{-8}$ - $10^{-7}$/°C range, primarily caused by thermal expansion of the spacer material.

A first realization of a FS-DFCB-OR set up for assessments of gas refractivity and density will be presented and its performance will be demonstrated. We will discuss how to design an FS-DFCB-OR system for optimal performance for assessments of gas refractivity and density.

9:40am **VT+MN-MoM5 Cold Cathode Gauge Improvements Extend Performance into UHV Pressure Range**, ***Timothy Swinney***, *G. Brucker*, MKS Instruments, Inc., Pressure and Vacuum Measurement Group

Cold cathode gauges (CCG) of inverted magnetron design are routinely used to measure pressure in industrial high vacuum chambers. Reduced internal outgassing, compared to hot cathode gauges, also makes CCGs well suited for accurate ultra-high vacuum (UHV) measurement in applications such as high-energy physics, surface science experiments and ultrahigh resolution mass spectrometers. In order to provide accurate and repeatable pressure measurements extending into deeper UHV levels, it is important to design CCGs that provide a consistent linear response to pressure over the entire measurement range. Our latest research efforts have focused on the understanding of gauge signal response to pressure with particular emphasis on the displacement of the magnetron knee and discharge sustain issues to lower pressures through systematic design changes. In this presentation, the linear response of CCGs to pressure is explained based on a simple pure electron plasma model. Pressure readings below the magnetron knee are described in terms of a pressure-dependent plasma model controlled by design parameters. The effect of magnetic strength, electric field and plasma boundary conditions on the onset of the magnetron knee and the ability to sustain a stable discharge into UHV levels is described. A patent-pending modification to the CCG internal electrode design is presented that extends the operational pressure of the gauge into deeper UHV levels by controlling the location of the pure electron plasma inside the ionization volume. This new understanding of CCG signal response to pressure has led to the development of enhanced sensor designs that operate at pressures one to two decades lower than legacy designs.

10:00am **VT+MN-MoM6 Sapphire MEMS based Capacitance Diaphragm Vacuum Gauge for 0-0.1Torr Operating at 200 °C**, ***Takuya Ishihara***, Azbil Corporation, Japan, *M. Sekine, M. Soeda, M. Nagata*, Azbil Corporation

To meet with downsizing of semiconductor device, various new manufacturing processes such as Atomic Layer Deposition (ALD) and Atomic Layer Etching (ALE), are put into practical use. In particular, ALE is a new atomic level etching technique, which can be applied to high aspect ratio structure or narrow slit . Conventionally, the pressure range of capacitance manometer for etching process is mainly 0-0.1Torr for reasons such as using inductively coupled plasma. And self-heating temperature of that is usually 45 °C, or at most 100 °C for the stabilization.

In this paper, authors have assumed that towards ALE process enhancement, etching would require high temperature process operation, such like 200 °C to prevent by-product from depositing inside of manometer in deposition step. Therefore, there is a motivation to develop capacitance manometer with its pressure range of 0-0.1Torr operating at 150-200 °C.

Entirely sapphire-based capacitive pressure sensor chips utilizing MEMS (Micro-Electro-Mechanical Systems) processes, which can be operated at 200 °C with from 0-1 to 0-1000 Torr pressure range have been developed by authors (Fig.1). To diminish pressure range to 0-0.1Torr, we need to reduce sensor diaphragm thickness to get sufficient sensitivity, but thinner diaphragm would be influenced heavily by noises, such like vibration from vacuum pumps, diaphragm sticking, and mechanical stress from sensor package and so on.

One of the critical issue is the zero point drift which was observed under back ground vacuum level after applied pressure over 100 °C (Graph.1). As a result of various verification experiments, this phenomenon was proved to be caused by the slight difference of temperature between sensor diaphragm surface and dilute gas in back ground vacuum. In other words, thermal energy exchange between diaphragm and gas results local expansion or shrinkage of the diaphragm because of its thinner thickness, which deform diaphragm (Fig.2). In our thermal simulation like Fig.3, only 0.05 °C temperature deference causes 0.5% Full Scale zero point drift at 0.1Torr range, which is fatal for the monitoring or controlling of the process. The temperature of the background gas depends on the temperature of inside wall of the process chamber which cannot be controlled by capacitance manometer itself. To solve this problem we have developed new sensor chip structure utilizing sapphire MEMS technology in which the process gas exchanges thermal energy with sensor chip before arriving to the diaphragm (Fig.4). By this new sensor chip, the zero point drift was suppressed to under 0.1% Full Scale, which is sufficient value to apply for the processes (Graph.1).

10:40am **VT+MN-MoM8 ROSINA/Rosetta: Exploring the Origin of our Solar System with Mass Spectrometry in Space**, ***Kathrin Altwegg***, University of Bern, Switzerland **INVITED**

On 30 September 2016 the European Space Agency's Rosetta spacecraft softly crash-landed on comet 67P/Churyumov-Gerasimenko and brought an intense period of more than 2 years of continuous investigation to an end. Rosetta data led to many discoveries about the origin of the material and the processing in our early Solar System. Among the payload instruments, ROSINA, the mass spectrometer suite, obtained fundamental properties of the comet by measuring the gases emanating from its nucleus.

Besides detecting many organic molecules never seen in space before, ROSINA was also able to measure precise isotopic abundances for noble gases, sulfur and silicon as well as D/H in water and H2S. By following the comet from 3.8 AU to perihelion and out again to 3.8 AU desorption patterns could be followed for individual species, allowing deeper insights into the nature of cometary ice. Some of the findings clearly point to unprocessed ice from the prestellar stage which allows to study chemistry in the presolar cloud more or less "in situ".

Some of the most important findings will be discussed in the presentation like the "zoo" of volatile and semi-volatile organics, the isotopic signature of Xenon and its relation with the terrestrial atmosphere.

11:20am **VT+MN-MoM10 Stabilization of Emission Current from Cold Field Emitters by Reducing Pressure to $10^{-10}$ Pa**, ***Keigo Kasuya***, *T. Ohshima, S. Katagiri, T. Kawasaki*, Hitachi, Ltd., Japan

In the presence of a strong electric field, electrons are emitted from sharply pointed cathodes at room temperature. This cold field emission (CFE) process provides a prominent electron beam with high brightness and a low energy spread, so CFE emitters are used extensively in a variety of electron microscopes.

One of the important challenges for CFE is stabilizing the emission current. The adsorption of residual gases on the emitter increases the surface work function and decreases the emission current over time. Additionally, surface sputtering by ions causes irregular current fluctuations.

One way to stabilize emission current is to reduce the pressure around the electron gun. This decreases incident gases and ions hitting the emitter and slows the current decrease. We reduced the pressure of an electron gun from $10^{-8}$ to $10^{-10}$ Pa by using non-evaporative getter (NEG) pumps [1]. This stabilized the emission current so that it was almost constant over a 24 hour period. The 90% decrease time, the time it takes the current to fall to 90% of the initial value, was increased from 10 minutes to 1280 minutes. In addition, the maximum emission current was increased from 30 μA to 1000 μA. With this gun, operators can use electron microscopes without the need for emission current adjustment.

By applying this technology, we developed a 1.2 MV high voltage transmission electron microscope [2]. The electron gun is equipped with a preaccelerator magnetic lens for enhancing the effective brightness of the electron beam. The pressure of the gun was $3X10^{-10}$ Pa, and a stable emission current was obtained. The microscope achieved the world's highest spatial resolution of 43 pm.

Part of this research was funded by a grant from the Japan Society for the Promotion of Science (JSPS) through the "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)," initiated by the Council for Science and Technology Policy (CSTP).

[1] K. Kasuya et al., J. Vac. Sci. Technol. B, 34, 042202 (2016).

[2] K. Kasuya et al., J. Vac. Sci. Technol. B, 32, 031802 (2014).

11:40am **VT+MN-MoM11 Measurement and Prediction of Quadrupole Mass Spectrometer Sensitivities**, ***Robert Ellefson***, REVac Consulting

Accurate analysis of partial pressure and gas composition by quadrupole mass spectrometry (QMS) requires measuring the QMS sensitivities and fragmentation factors for gas species of interest. The sensitivity is the ratio of ion current for the species to the partial pressure of that species. Fragmentation factors are ratios of fragment [#] ions to the parent ion and are used to correct for species interference at the fragment mass. Measurement with pure gases of each species is the traditional method for determining sensitivities and fragmentation factors; this involves a significant investment in gases and delivery hardware. The QMS ion source operates in the molecular flow regime so that for each species, gas flow is independent of other components present. This allows known mixtures of species to be used for independently measuring multiple species sensitivities. Data using two designed mixtures are presented giving sensitivities and fragmentation ratios for nine species: $H_2$, He, $H_2O$, $N_2$, $O_2$, Ar, $CO_2$, Kr and Xe. Gases are delivered to the QMS with a molecular flow inlet system which delivers a broad range of predictable partial pressures for species. Sensitivity versus partial pressure determines the range of linear operation of the QMS indicated by constant sensitivity for that species over a range of pressure. A model for predicting QMS sensitivities for species not measured is also presented. The model uses the QMS sensitivities for the known gas species analyzed to determine the parameters for predicting the sensitivity of an unknown. The factors of the model are: 1. A calculated [#] ionization cross section as a function of incident electron energy data from the NIST Web Book, 2. The mass spectrum of the gas from the Web Book, 3. A model for ion transmission as a function of mass for the QMS in use, and, 4. The QMS sensitivity for $N_2$ as a reference point to capture the ion source geometry and unique behavior of the QMS under test. Examples of the predictive method and estimated uncertainty are given.

## 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.

S. Beniwal, J. Hooper, D. P. Miller, P. S. Costa, G. Chen, S.-Y. Liu, P. A. Dowben, E. C. H. Sykes, E. Zurek, and A. Enders, "Graphene-like Boron–Carbon–Nitrogen Monolayers," *ACS Nano*, vol. 11, no. 3, pp. 2486–2493, Mar. 2017.

## Actinides and Rare Earths Focus Topic
## Room: 22 - Session AC+AS+SA+SU-MoA

### Chemistry and Physics of the Actinides and Rare Earths
### **Moderator:** David Shuh, Lawrence Berkeley National Laboratory

1:40pm **AC+AS+SA+SU-MoA1 Oxidation and Crystal Field Effects in Uranium**, ***James G. Tobin***, University of Wisconsin-Oshkosh, *S.W. Yu,* Lawrence Livermore National Laboratory, *C.H. Booth,* Lawrence Berkeley National Laboratory, *T. Tyliszczak,* Lawrence Berkeley Lab, University of California, Berkeley, *D.K. Shuh,* Lawrence Berkeley National Laboratory, *G. van der Laan,* Diamond Light Source, UK, *D. Sokaras, D. Nordlund, T.C. Weng,* Stanford Synchrotron Radiation Lightsource, *P.S. Bagus*, University of North Texas

An extensive investigation of oxidation in uranium has been pursued. [1] This includes the utilization of soft x-ray absorption spectroscopy, hard x-ray absorption near-edge structure, resonant (hard) x-ray emission spectroscopy, cluster calculations, and a branching ratio analysis founded on atomic theory. The samples utilized were uranium dioxide ($UO_2$), uranium trioxide ($UO_3$), and uranium tetrafluoride ($UF_4$). A discussion of the role of nonspherical perturbations, i.e., crystal or ligand field effects, will be presented. The conclusions are as follows. (1) The hypothesis of the potential importance of CF effects in the XAS branching ratio (BR) analysis of 5f states was incorrect. (2) Both $UO_2$ and $UF_4$ are $n_{5f} = 2$ materials. The combination of the 4d XAS BR and RXES analyses is particularly powerful. (3) CF broadening in the $L_3$ RXES spectroscopy does not preclude a successful analysis. (4) The prior experimental result that $n_{5f}$ ($UO_2$) = 3 and the proposed causation by covalent bonding was incorrect. $UO_2$ is an n5f = 2 material and analysis within a simple, ionically localized picture provides the correct result. (5) $UO_3$ appears to be an $n_{5f} = 1$ material. (6) While the 4d XAS BR analysis is blind to CF effects, crystal field and covalence remain important. (7) For localized actinide systems, the 4d XAS BR analysis founded upon the utilization of the intermediate coupling scheme remains a powerful tool. (8) For delocalized actinide systems, the BR analysis is problematic.

[1] J. G. Tobin, S.-W. Yu, C. H. Booth, T. Tyliszczak, D. K. Shuh, G. van der Laan, D. Sokaras, D. Nordlund, T.-C. Weng, and P. S. Bagus, Phys. Rev. B **92**, 035111 (2015)

2:00pm **AC+AS+SA+SU-MoA2 Electron Spectroscopy Studies of U and U-Mo Hydrides**, ***Ladislav Havela***, *M. Paukov, M. Dopita, L. Horak, M. Divis, I. Turek*, Charles University, Prague, Czech Republic, *T. Gouder, A. Seibert, F. Huber*, European Commission, Joint Research Centre, Karlsruhe, Germany, *D. Legut*, VSB - Technical University of Ostrava

U hydride was the first material indicating that 5*f* states can yield ferromagnetism analogous to 3*d* metals. However, the electronic structure of $UH_3$ is not yet well understood, and it is not clear to which extent it can be described by conventional band structure calculations. We have been studying structure and electronic properties of $UH_3$ and $(UH_3)_{1-x}Mo_x$ films synthesized by reactive sputtering. Primary diagnostics was performed by in-situ XPS. The U-4*f* core level spectra exhibit a development as a function of partial pressure of $H_2$ in Ar ($p_{Ar} = 8*10^{-3}$ mbar). Their intensity gradually decreases, they shift by 0.2 eV towards higher binding energies (BE) and an extended (9 eV wide) satellite structure develops on the high BE side of both 4*f* peaks. This tendency saturates at 5% $H_2$ concentration, and we assume that this pressure is sufficient to form $UH_3$. XRD and X-ray reflectivity proved indeed the $\beta$-$UH_3$ structure of deposited films, which were polycrystalline, but highly textured. Ferromagnetism of the $UH_3$ films has the correct Curie temperature $T_C \approx 165$ K. Magnetic coercivity of the films is enormous, the width of hysteresis loop exceeds 10 T at low temperatures. Details of the valence band observed in UPS reveal a transformation of the triangular emission of the U metal into a sharp feature at the Fermi level accompanied by a broad shoulder around 0.5 eV for the hydride. A distinct development was noticed also for the U-6*p* states, which become narrower and shift by 1.2 eV to higher BE in the hydride, which can be interpreted as an impact charge transfer from U towards H. Besides photoelectron spectroscopy, the variations of electronic states were monitored also by BIS spectra collected for the 1486.6 eV photon energy. The spectroscopy results are confronted with different types of in-initio calculations.

As U-Mo alloys tend to form nanocrystalline $\beta$-$UH_3$ based hydrides, we were curious about reactive sputter deposition of the U-Mo alloys. We found that the tendency to form hydrides is fast suppressed by Mo for room temperature sputtering ($\gamma$-U alloy without H is the product), but cooling the substrate to 77 K helps to maintain the hydride phase even for even higher Mo concentrations.

This work was supported by the Czech Science Foundation under the grant No. 15-01100S.

2:20pm **AC+AS+SA+SU-MoA3 Comparative Structural Studies of Tetravalent f ions in Solids and in Aqueous Solutions**, ***Lynda Soderholm***, Argonne National Laboratory **INVITED**

Predicting a metal ion's aqueous chemistry – including its stability, reactivity, and solubility – requires molecular-level knowledge of the various factors influencing speciation and complex formation. This chemistry is particularly complicated for f-ions, where the electrostatic, non-directional bonding provides flexibility to their coordination environments, which can vary widely depending on the ligating species. This presentation will focus on our efforts to establish trends in f-ion solution behavior and to provide a direct link between metal correlations in solution and the thermodynamic stability constants that are used to derive relative free energies of available metal-ligand complexes. Although several examples will be provided, the discussion will center on a comparison between the behaviors of tetravalent Th, Pu, and Ce and how differences in the complexes formed in solution impact the composition and structure of precipitates that form. High-energy X-ray scattering (HEXS) experimental results will be used to demonstrate how changing conditions can influence solution chemistry, with a specific emphasis on the role of the anion. X-ray surface-based techniques will be used to provide a link between solution speciation and the complexes that form on mineral surfaces. The structures of molecular species isolated as single-crystals from these solutions will be directly compared with the solution and surface-adsorbed species. This work is supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences, Biosciences and Geosciences, Heavy Element Chemistry, under contract No. DE-AC02- 06CH11357.

4:00pm **AC+AS+SA+SU-MoA8 Interfacial Dynamics in Radiation Environments and Materials: An Energy Frontier Research Center**, ***Sue Clark***, Pacific Northwest National Laboratory **INVITED**

The US Department of Energy's Office of Environmental Management (EM) is faced with remediating millions of liters of highly radioactive wastes that resulted from the production of nuclear weapons during the Cold War. These legacy wastes are stored in large, underground tanks at former nuclear weapons production sites in the US. Not only are these wastes radioactive, but they are also highly alkaline and concentrated in electrolytes. Using currently available technologies and approaches. EM estimates that processing these wastes into waste forms for disposal in a geologic repository will take at least 5 decades and over $300 billion dollars. Basic research on the chemical and physical behavior of these materials in such extreme conditions is needed to provide a foundation of innovation to accelerate processing and reduce aggregate costs.

IDREAM is an Energy Frontier Research Center (EFRC) conducting fundamental research to support innovations in processing high-level radioactive wastes (HLW). Activities in IDREAM are designed to support the transformation of HLW processing by elucidating the basic chemistry and physics required to control and manipulate interfacial phenomena in extreme HLW environments (e.g., non-equilibrium, heterogeneous, and chemically complex). This foundational knowledge is required to achieve IDREAM's vision to master molecular–to–mesoscale chemical and physical phenomena at interfaces in complex environments characterized by extremes in alkalinity and low-water activity, and driven far from equilibrium by ionizing (g,b) radiation. Further, understanding these processes will enable prediction of waste aging over the many decades required to complete this difficult cleanup task.

Currently, IDREAM activities focus on the aluminate anion in alkaline solutions, and its nucleation into boehmite (aluminum (oxy)hydroxide, AlO(OH)) and gibbsite (aluminum hydroxide, $Al(OH)_3$) , as they are key principal components of bulk waste materials to which a variety of other metal ions and radionuclides partition. In this presentation, initial results on interfacial reactivity between aluminate, boehmite, and gibbsite will be discussed. The impact of g and b radiation on boehmite and gibbsite will also be presented.

4:40pm **AC+AS+SA+SU-MoA10 Real Structure of Nanocrystalline Uranium based Hydrides Studied By the X-ray Scattering Methods**, ***Milan Dopita***, *L. Havela, L. Horak, M. Paukov*, Charles University, Prague, Czech Republic, *Z. Matej*, MAX-IV, Lund, Sweden

Interaction of hydrogen with uranium is not only an important issue for its nuclear and military applications but also contributes to understanding of the 5*f* magnetism. Uranium hydrides provide a unique tool to observe an impact of expansion of the U lattice, allowing formation of U moments and their ferromagnetic ordering. However, the electronic structure of uranium hydrides is not fully understood yet. Especially, the role of the real structure, i.e. the influence of the lattice defects, particle size in the nanocrystalline bulk materials and the preferred orientation of crystallites – the texture, the strains and stresses in the case of films is not well described, but can significantly influence electronic and magnetic properties of materials.

In our contribution we report the real structure of bulk and powder Mo- and Zr-alloyed uranium hydrides, prepared by rapid (splat) cooling and high pressure synthesis, and Mo alloyed uranium hydride films synthesized by reactive sputtering, using X-ray scattering methods. The sample series with different alloying element concentration as well as at different hydrogen pressure were prepared. Since the classical powder diffraction methods, as the profile analysis and/or Rietveld method, reach the limits of their applicability for the nanocrystalline uranium hydrides alloys in terms of the real structure description, the use of more advanced methods is necessary. Here we describe the total scattering method – pair distribution function analysis, and Debye equation calculation for simulations of the intensity scattered from nanocrystalline clusters.

The key results of our study were the determination of the phase composition and its evolution, as well as detailed atomic positions, which can influence the U-U spacings in individual phases, tuning the 5*f* magnetism. The methods are able to describe the particle size and defect distributions, the stress, strains, and textures in the films. In addition, the depth profiles and evolution of above mentioned parameters can be determined. Such X-ray analysis provides useful characterization of the sputter-deposited films, which are also used for fundamental electron spectroscopy studies of $UH_3$-based films, exhibiting much lower surface contamination by oxygen than comparable bulk material.

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

## Applied Surface Science Division
## Room: 13 - Session AS+BI-MoA

### Practical Surface Analysis: Complex, Organic and Bio-systems
**Moderators:** Scott Lea, Pacific Northwest National Laboratory, Paulina Rakowska, National Physical Laboratory, UK

2:00pm **AS+BI-MoA2 Environmental Charge Compensation - Near Ambient Pressure XPS as a Tool for Surface Chemical Analysis of Iinsulators without Charging Effects**, ***Paul Dietrich***, *A. Thissen,* SPECS Surface Nano Analysis GmbH, Germany, *S. Bahr*, Enviro Analytical Instruments GmbH, Germany

Since many decades XPS (or ESCA) is the well-accepted standard method for

non-destructive chemical analysis of solid surfaces. To fulfill this task existing ESCA tools

combine reliable quantitative chemical analysis with comfortable sample handling concepts,

integrated into fully automated compact designs.

Generically insulators will positively charge in XPS due to the irradiation with X-rays and

the emission of photoelectrons. Without compensation this effect leads to strong continuous

shifts and asymmetric line shapes of the emission lines in the spectra. To perform an exact

characterization and quantification of strongly insulating materials different concepts of

charge compensation or neutralization have been developed over the last decades. A short

overview is given starting from low energy electrons offered from so-called "flood guns" or

other sources, via compensation by a combination of electrons and ions to rare methods like

illumination with visible light during the analysis and compensation by the produced

electron-hole pairs. The opportunities and challenges of the different methods are compared.

The development of XPS method towards environmental or (near) ambient pressure

working conditions has revolutionized this method regarding applications. In-situ and

in-operando measurements in pressure of up to and above 25mbar are easily possible, even

with laboratory based systems and using EnviroESCA even in a standard analytical tool.

During the last months, measurements on insulators have shown, that they can be measured

with exception in surrounding pressures of a couple of mbar without any charging. This new

technique of charge neutralization is neamed Environmental Charge Compensation (ECC).

This presentation summarizes results of measurements on insulating polymer samples,

showing the resulting spectroscopic resolution for C1s and O1s emission lines. A

comparison for PET and PTFE to other neutralization techniques is given. In addition

measurements on bulk insulators from polymeric materials, ceramics, food samples, aqueous solutions, stones, soil and even zeolites are shown, that cannot easily be obtained in

UHV based XPS systems.

Furthermore the effect is described in detail, including the influence of pressure and gas

composition on the charge neutralization. An outlook is presented towards completely new

resulting fields of application of XPS, when combined with ECC.

2:20pm **AS+BI-MoA3 Does Time Play a Role in Glyoxal and Hydrogen Peroxide Photochemical Aging?**, ***Fei Zhang***, *X.F. Yu, X. Sui,* Pacific Northwest National Laboratory, *J.M. Chen,* Fudan University, *Z.H. Zhu, X.Y. Yu*, Pacific Northwest National Laboratory

Aqueous surfaces consisting of glyoxal and hydrogen peroxide ($H_2O_2$) after photochemical aging have been studied in a microfluidic reactor (System for Analysis at the Liquid Vacuum Interface, SALVI) by in situ liquid Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Positive and negative ion mode mass spectra provide complementary information of the surface reactions. Compared with previous results using bulk solutions, our unique liquid surface molecular imaging approach makes it possible to observe glyoxal hydration (i.e., first and secondary products, hydrates), oxidation products (i.e., glyoxylic acid, oxalic acid, formic acid, malonic acid, tartaric acid), oligomers (i.e., $C_7H_{11}O_9^+$, $C_6H_5O_{10}^-$), water clusters (i.e., $(H_2O)_nH^+$, n< 43, $(H_2O)_nOH^-$, n< 44), and cluster ions (i.e.,$C_6H_{17}O_{12}^+$, $C_7H_9O_{11}^-$) with submicrometer spatial resolution. Spectral principal component analysis (PCA) is used to determine similarities and differences among photochemical aging samples ranging from 15 minutes to 8 hours. The oxidation products such as glyoxylic acid, glycolic acid, and tartaric acid tend to peak at around between 30 min and 1 h. UV aging; while oligomers and large water clusters (i.e., $(H_2O)_{22}OH^-$, $(H_2O)_{23}OH^-$,$(H_2O)_{24}OH^-$) form significantly at about 3 h. The oligomer formation reaches its maximum at 4 h., and reduces afterwards. Large water clusters (n> 15) become more significant as photochemical aging progresses, indicating more hydrophobicity at the aqueous surface as predicted by molecular dynamic simulation in earlier works. SIMS three-dimensional (3D) chemical mapping enables visualization of the surface mixing state at the molecular level. We have presented the temporal progression of the 3D surface mixing state of various products from glyoxal and hydrogen peroxide oxidation for the first time. Such physical measurements pave a new way to investigate complex surface reaction mechanisms as an important source of aqueous secondary organic aerosol (SOA) formation in atmospheric chemistry.

2:40pm **AS+BI-MoA4 Study of Drug Uptake and Action on Metabolic Processes at the Single-Cell Level using the 3D OrbiSIMS**, ***Ian S. Gilmore***, *M.K. Passarelli, M. Lorenz,* National Physical Laboratory, UK, *C.F. Newman, P.S. Marshall, A. West,* GlaxoSmithKline, UK, *P.D. Rakowska, R. Havelund, C.T. Dollery*, National Physical Laboratory, UK

A major quest for the pharmaceutical industry is the reduction of late-stage drug failure. Measurements that can identify future failure at the early stages of drug development are therefore of great importance. This requires label-free imaging of the distribution of pharmaceutical compounds and metabolites with subcellular resolution. We have previously shown [1] that ToF-SIMS can provide useful sub-cellular resolution images but analysis is limited by insufficient mass accuracy, mass resolving power for accurate identification of metabolites and sensitivity.

We have recently led the development of a powerful new hybrid instrument, the 3D OrbiSIMS [2], combining an Orbitrap$^{TM}$-based Thermo Scientific$^{TM}$ Q Exactive$^{TM}$ HF instrument and a dedicated ToF-SIMS 5. The instrument is equipped with high-resolution ion beams including a new micrometre resolution argon cluster ion beam for biomolecular imaging and 3D analysis of organics and an ultra-high resolution Bi cluster focussed ion beam with < 200 nm resolution.

In this study, we demonstrate the unparalleled ability for 2D and 3D metabolite imaging with sub-cellular resolution. We show significant variability of drug uptake at the single cell level and demonstrate direct evidence of up regulation of metabolites. This can only be revealed with a single-cell study. Furthermore, we demonstrate a new method for in situ matrix deposition for 3D imaging that significantly increases sensitivity. This is especially important for current drug candidates with Log P values ≤ 3 (Lipinski rule of five), which are known to have low molecular secondary ion yields. [3]

[1] M.K. Passarelli et al, Analytical chemistry 87 (13), 2015, 6696

[2] M.K. Passarelli et al, submitted, 2017

[3] J.L. Vorng et al, Analytical Chemistry 88 (22), 2016, 11028

3:00pm **AS+BI-MoA5 TOF-SIMS Cluster Beam Depth Profiling and 3D Imaging of Oral Drug Delivery Films**, ***Greg Gillen***, *S. Muramoto, J. Staymates, E. Robinson*, NIST

Dissolvable oral thin film (OTF) drug delivery systems are gaining increased interest as convenient alternatives to more conventional tablets and capsules for drug delivery applications. The OTF's are typically made by mixing an active pharmaceutical ingredient (API) into a dissolvable polymer that is administered to the patient by placing under the tongue or against the inside of the cheek. Direct adsorption of the API into the systemic circulation bypasses gastrointestinal delivery and can provide higher levels of bioavailability and a more rapid release profile in appropriate medications. One critical challenge with further development of OTF drug delivery systems is the lack of appropriate measurement tools for the characterization of API concentration, phase and dose uniformity throughout the depth of the polymer film (typically ~100 um in thickness). Furthermore, OTF's are currently manufactured as bulk sheets with fixed levels of API. This is a significant roadblock to realization of OTF's for personalized medicine where there is a growing interest in manufacturing of OTF's with individualized and patient-specific API dosages. One promising method of production of such films that is currently being explored in our laboratory is the used of drop on demand inkjet printing to precisely deposit individualized API doses onto prefabricated films.

In this work, we explore the utility of Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) using gaseous cluster ion beam (GCIB) depth profiling for the characterization of the lateral and in-depth distribution of API's in model OTF films. Three types of films were examined; (1) model thin films of pullulan, (2) model thin films of pullulan that had been dosed using drop on demand inkjet printing with various concentrations of relevant API's and (3), commercially available OTF films (single and multilayer films) containing the anti-opioid medications buprenorphine and naloxone which are widely used medications for treatment of opioid dependency. Cluster SIMS depth profiling was able to resolve compositional differences throughout the depth of each of these films (>70 um in thickness) and localize the individual API's. Furthermore, the ability to characterize the lateral and in depth distribution of API's in individual inkjet droplets will be demonstrated as well as the use of inkjet printing to prepare in situ concentration standards for evaluation of dosage variability. Finally, we also demonstrate the use THz Raman imaging for chemical identification of the API and possible phase changes due to the use of inkjet-printed formulations.

3:20pm **AS+BI-MoA6 Characterisation of Bioelectronic Material Surfaces using Surface Spectroscopies**, ***Sarah Coultas***, Kratos Analytical Limited, UK, *W. Boxford,* Kratos Analytical Ltd, UK, *C.J. Blomfield,* Kratos Analytical Limited, UK, *M. Firlak, J. Hardy,* Lancaster University, UK

Electromagnetic fields affect a variety of tissues (e.g. bone, muscle, nerve and skin) and play important roles in a multitude of biological processes. This has inspired the development of electrically conducting devices for biomedical applications, including: biosensors, drug delivery devices, cardiac/neural electrodes, and tissue scaffolds. It is noteworthy that there are a number of clinically approved devices capable of electrical stimulation of the body, all of which are designed for long term implantation. The first examples were developed in Sweden and include bionic eyes, ears and electrodes for deep brain stimulation (DBS). Recently there has been considerable industrial interest in the development and commercialisation of bioelectronic medicines. Bioelectronics is an emerging area of technology that promises broad impact in healthcare.

The detailed analysis of biomaterials and biomedical devices offers valuable insight into the underlying function of the products. The materials are composites of electroactive polymers (e.g. polypyrrole) and biopolymers (e.g. polysaccharides and proteins) that can be used for various applications (e.g. drug delivery, tissue scaffolds).

Here we demonstrate the application of surface spectroscopies, including XPS and UPS, to characterise bioelectronic materials in various morphologies (e.g. films and foams). We utilise a range of approaches to fully characterise the materials, including investigating any variations in composition either laterally or with depth. We also explore the usefulness of surface cleaning using Argon clusters.

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4:00pm **AS+BI-MoA8 High-resolution SIMS Imaging of Subcellular Structures**, ***Mary Kraft***, *A.N. Yeager,* University of Illinois at Urbana-Champaign, *P.K. Weber,* Lawrence Livermore National Laboratory **INVITED**

In mammalian cells, lipids and cholesterol form the selectively permeable plasma membrane that separates the cell from its surroundings, and the intracellular membranes that delineate the boundaries of organelles and transport vesicles. The distributions of cholesterol and each lipid species between these organelles is correlated with health and disease. The accumulation of cholesterol and certain lipid species within lysosomes and endosomes causes defects in intracellular trafficking that can be fatal if left untreated. The ability to image the relative abundances of cholesterol and distinct lipid species within intracellular compartments could lead to a better understanding of the biological mechanisms that regulate subcellular lipid distribution. For this purpose, we have combined metabolic stable isotope incorporation with secondary ion mass spectrometry (SIMS), which is performed on a Cameca NanoSIMS 50, to image the intracellular distributions of cholesterol and sphingolipids. By using depth profiling SIMS to image the distributions of $^{18}$O-cholesterol and $^{15}$N-sphingolipids within a portion of a Madin-Darby Canine Kidney (MDCK) cell, we determined that these two components are enriched within separate intracellular compartments. The sizes and relative positions of the $^{15}$N- and $^{18}$O- enriched intracellular features that are visible in the 3-D representations of the SIMS images suggest that the $^{15}$N-sphingolipids are located within transport vesicles, whereas the $^{18}$O-cholesterol seem to be concentrated within lipid droplets.

4:40pm **AS+BI-MoA10 EnviroESCA – Routine Surface Chemical Analysis under Environmental Conditions For Biological Samples**, ***Andreas Thissen**, P. Dietrich,* SPECS Surface Nano Analysis GmbH, Germany, *S. Bahr,* Enviro Analytical Instruments GmbH, Germany, *M. Kjaervik, W. Unger,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany

Since many decades XPS (or ESCA) is the well-accepted standard method for

non-destructive chemical analysis of solid surfaces. To fulfill this task existing ESCA tools

combine reliable quantitative chemical analysis with comfortable sample handling concepts,

integrated into fully automated compact designs.

Over the last years it has been possible to develop XPS systems, that can work far beyond

the standard conditions of high or ultrahigh vacuum. Near Ambient Pressure (NAP) XPS has

become a fastly growing field in research inspiring many scientist to transfer the method to

completely new fields of application. Thus, by crossing the pressure gap, new insights in

complicated materials systems have become possible using either synchrotron radiation or

laboratory X-ray monochromators as excitation sources under NAP condtions.

Based on this experience SPECS Surface Nano Analysis GmbH has developed a

revolutionary tool to realize the long existing dream in many analytical laboratories:

reproducible chemical surface analysis under any environmental condition. EnviroESCA

allows for different applications, like extremely fast solid surface analysis of degassing (but

also non-degassing) samples, ESCA analysis of liquids or liquid-solid interfaces, chemical

analysis of biological samples, materials and device analysis under working conditions.

After introduction of the technological realization a comprehensive survey of results will be

given starting from standard solid conductive samples under different pressure conditions,

bulk insulators with environmental charge compensation applied, high throughput analysis

of batches of similar objects, geological samples, chemical analysis of pharmaceuticals to

the comparative analysis of ultrapure liquid water with different aqueous solutions.

The application of Near Ambient Pressure XPS to biological specimen from plants and

animals, biofilms and bacteria, as well as food samples is a completely new field for

electron spectroscopic studies of the surface chemical composition.

An outlook is presented on the application to electrochemical and other in-operando devices.

Finally the influence of the ambient conditions on quantification in XPS will be

demonstrated and discussed.

This project has received funding from the EMPIR programme co-financed by the Participating

States and from the European Union’s Horizon 2020 research and innovation programme.

## Spectroscopic Ellipsometry Focus Topic
## Room: 9 - Session EL+AS+EM-MoA

### Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches
### **Moderator:** Maria Losurdo, CNR-NANOTEC

1:40pm **EL+AS+EM-MoA1 Temperature Dependent Mueller Matrix Measurements of Magnetised Ni near the Curie Temperature**, ***Farzin Abadizaman***, *S. Zollner*, New Mexico State University

The temperature dependence of the optical constants of the magnetized bulk Ni demonstrates an anomaly near the Curie temperature. We investigate this anomaly by taking a measurement of the temperature dependent Mueller Matrix (MM). Using spectroscopic ellipsometry at an energy 1.96 eV, the MM measurement was taken from 350 K to 500 K with 10 K steps, and from 500 K to 670 K with 1 K steps, and from 670 K to 730 K with 10 K steps.

In order to distinguish the anisotropic properties of the magnetized Ni from the windows effects, three samples (Ge, Ni, and $SiO_2$ on Si) were measured inside the cryostat in the energy range from 1 eV to 5 eV with 0.1 eV steps. The results show that the anisotropic elements of the MM behave in the same fashion for all samples, except for element $M_{24}$,which depends on the sample.

The MM data of magnetized Ni indicate very small changes in the anisotropic portion of the MM compared to the windows effect. The authors believe that these changes are due to the magneto-optical Kerr effect. However, since a rotating-analyzer ellipsometer was used, the last row of the MM is absent and a complete MM measurement needs to be performed to find the magneto-optical Kerr effect in the other anisotropic elements too.

However, very large decreases in the isotropic MM elements were found near the Curie temperature. This means, the changes in optical constants near Tc are due to the on-diagonal Drude part of the dielectric tensor, which can be explained by s- to d-band electron-phonon scattering above and below $T_c$. These changes are absent when decreasing the temperature and for unmagnetized Ni.

2:00pm **EL+AS+EM-MoA2 Ellipsometry Based Observation of Material Ordering Process in Holography**, ***Hao Jiang***, *H. Peng, Y. Liao, S. Liu*, Huazhong University of Science and Technology, China

Ordered materials with superior performance have been constantly pursued. Nevertheless, the direct, precise and non-destructive observation of the ordering process, which is especially critical for continuous manufacturing, remains a formidable challenge. Herein, we introduce Mueller matrix ellipsometry (MME) as a nondestructive method to quantitatively observe the material ordering process during holography. This non-destructive observation directly offers the exact width, refractive index, nanoparticle weight fraction and volume fraction in each constructive (bright) or destructive (dark) interference area, which is impossible to be implemented using other existing techniques. Meanwhile, the width of dark region is observed to decrease while the width of bright region increases with an augmentation of the holographic recording time, distinct from previous assumption. More importantly, an apparent diffusion coefficient of $1.3\times10^{-15}$ $m^2$ $s^{-1}$ is determined on the basis of recording time-dependent grating structure observation, which is 3 orders of magnitude lower than the Stokes-Einstein prediction. The distinct diffusion coefficient is regarded to be the result of competition between the forth diffusion driven by the chemical reaction and backward diffusion arising from nanoparticle concentration gradient. This novel protocol is envisioned to pave the way for precisely and non-destructively understanding the ordered structure formation in electrics, photonics, photovoltaics, biomaterials and other disciplines.

2:20pm **EL+AS+EM-MoA3 Coherence in Polarimetry and Ellipsometry: Synthesizing Mueller Matrices in an Ellipsometer**, ***Oriol Arteaga***, Departament de Física Aplicada, Universitat de Barcelona, Spain **INVITED**

Interference phenomena are ubiquitous in optics and are the basis of the industry behind thin film optical coatings or thin film thickness measurements with ellipsometry. The interference of polarized beams was experimentally understood in 1819 when Arago and Fresnel derived the four laws governing the interference of polarized light. While spectroscopic ellipsometry provides information based on the position and number of interference oscillations in thin films, typically one has no macroscopic control of the beams that coherently superpose.

In this work we present a polarimetric analysis of an analogue of Young's double slit experiment that allows merging beams in a well-controlled manner. The experiment is analyzed with a new formalism that is useful to describe optical coherence and polarization and that shows that the superposition of two macroscopically distinguishable beams can be an effective method to experimentally synthesize Mueller matrices with on-demand polarization properties. This offers the opportunity of working with "synthesized" optical elements that behave just like "real" ones. We will discuss how this method can have a practical application in the construction of ellipsometers or polarimeters.

3:00pm **EL+AS+EM-MoA5 Femtosecond Spectroscopic Ellipsometry on Optoelectronic Materials and Photonic Structures**, ***Mateusz Rebarz***, *S.J. Espinoza,* ELI Beamlines - Czech Academy of Science, Czech Republic, *S. Richter, O. Herrfurth, R. Schmidt-Grund,* Universität Leipzig, Germany, *J. Andreasson,* Chalmers University of Technology, Sweden, *S. Zollner*, New Mexico State University

The ongoing progress in miniaturization and operational rates of electronic and optoelectronic devices obliges materials scientists to deeply understand the dynamics of the carriers upon external electromagnetic stimulus in very short time scale. Some phenomena such as scattering of electrons and phonons as well as recombination processes can be as short as tens of femtoseconds. All these processes affect the temporal and local dielectric constants and determine many operational parameters of the devices. In this work, we report on recent progress in developing a spectroscopic ellipsometer for characterization of ultrafast dynamic changes of dielectric properties in materials and photonic structures technologically relevant in optoelectronics. Our time-resolved ellipsometer is based on pump-probe technique and offers monitoring the time evolution of the dielectric properties in range 0-5 ns with time resolution ~100 fs in broadband spectral range (340-750 nm).

We present here the results of the measurements performed on Ge samples in comparison with theoretical predictions. Ultrafast phenomena such as excitation, relaxation and diffusion of charge carriers, band-gap renormalization and excitons screening will be discussed. In addition we report on the first data obtained from a ZnO-based planar microcavity especially on the temporal evolution of the microcavity modes. The time evolution of the ellipsometric parameters in the spectral range around the exciton-polariton mode will be discussed. We observed that such modes disappear upon the excitation, possibly due to screening of the excitons and re-appear after a few hundreds of femtoseconds as blueshifted modes. The investigation of the short-time dynamics of such modes can stimulate new theoretical approaches for the description of exciton-polariton systems.

3:20pm **EL+AS+EM-MoA6 Temperature Dependence of the Dielectric Function and Interband Critical Points of Bulk Germanium**, ***Carola Emminger***, *N. Samarasingha, F. Abadizaman, N.S. Fernando, S. Zollner*, New Mexico State University

Exploration of the optical properties of bulk germanium (Ge) is necessary for the advancement of Ge technology. In fact, many of the Ge applications depend on the dielectric function ($\varepsilon$), which is directly related to the electronic band structure. Here we investigate the effect of temperature on the optical properties and interband critical points (CPs), primarily the $E_0$ and $E_0+\Delta_0$ critical points of bulk Ge in the temperature range from 10 to 738 K using spectroscopic ellipsometry at 70° angle of incidence. The data was taken in two parts, in the near IR region and in the UV region, which provides data from 0.5 to 6.2 eV. The low temperature environment was created in a UHV cryostat with liquid helium and nitrogen as cryogens. To reduce the thickness of the native $GeO_2$ layer, the Ge sample was cleaned using ultra-pure water, isopropanol, an ultrasonic bath and ozone cleaning. It was possible to reduce the oxide thickness to about 11 Å at room temperature.

The authors used a two-phase model ($GeO_2$ layer/Ge substrate) and a parametric oscillator model with a set of adjustable parameters to extract the real and imaginary parts of the complex dielectric function of the bulk Ge for the whole temperature range. To investigate this temperature dependence of the CP parameters (threshold energy, broadening and phase angle) further, we also compared the second derivative $d^2\varepsilon/d^2\omega$ of the dielectric function with analytical line shapes.

The temperature has a significant influence on both the real and imaginary parts of the complex dielectric function of bulk Ge. This temperature dependent $\varepsilon$ can be explained by a Bose-Einstein occupation factor. Due to the electron-phonon interaction, we find a temperature dependent red shift (shift to lower energies) of the $E_0$ and $E_0+\Delta_0$ critical point energies. The temperature independent spin orbit splitting $\Delta_0$ is found to be 286 meV. A similar effect has been seen in the $E_1$, $E_1+\Delta_1$, $E_0^{'}$, and $E_2$ CP energies. These CPs are broadened and shifted to the lower energies with increasing temperature.

4:00pm **EL+AS+EM-MoA8 VUV Magneto-Optical Transient Ellipsometer**, ***Shirly Espinoza***, *J. Andreasson*, Institute of Physics ASCR, Czech Republic

This talk is about the ELIps instrument, an instrument that combines three advanced techniques of ellipsometry: VUV ellipsometry, Transient (Pump-probe) ellipsometry, and Magneto-optical ellipsometry [1].

The ELIps instrument allows users to work in a very wide range of energies from 1 eV to 40 eV. For measurements in the 1 eV to 6.5 eV range, it uses a transmission polarizer and analyzer combination. Meanwhile, for measurements in the 6.5–40 eV range, it uses a triple-reflection polarizer and analyzer combination. All the components are contained within a single UHV chamber designed with several additional ports to support future upgrades. For time resolved measurements in the VUV range the instrument will be used together with a high intensity High Harmonics Generation (HHG) source.

Time-resolved transient measurements of the optical properties of materials can be performed in the range of a few femtoseconds to nanoseconds. Initial experiments with transient absorption and transient ellipsometry in the NIR-UV range is being performed on proton-conducting materials for solid oxide fuel cell applications.

Additionally, ELIps is equipped with a Helmholtz coil, which allows the studies of the transverse magneto-optical Kerr effect on the sample, and with a cryostat for measurements at different temperatures.

Where is this instrument located? ELIps is in Prague, Czech Republic, at the European Extreme Light Infrastructure Beamlines (ELI Beamlines), a user facility project that will hold some of the most intense lasers in the world. It will open to the public on January 2018.

References

[1] S. Espinoza, G. Neuber, C. D. Brooks, B. Besner, M. Hashemi, M. Rübhausen and J. Andreasson. 2017. User oriented end-station on VUV pump-probe magneto-optical ellipsometry at ELI beamlines. *Applied Surface Science*. Published online. doi:10.1016/j.apsusc.2017.02.005

Acknowledgements

This work was supported by the project ELI – Extreme Light Infrastructure – phase 2 (CZ.02.1.01/0.0/0.0/15_008/0000162) and ELIBIO (CZ.02.1.01/0.0/0.0/15_003/0000447) from the European Regional Development Fund.

4:20pm **EL+AS+EM-MoA9 Infrared Ellipsometric Spectroscopy of $Hg_{1-x}Cd_xTe$ Bulk Samples**, ***Yanqing Gao***, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, China

**The infrared spectroscopic ellipsometry of $Hg_{1-x}Cd_xTe$ ($x$=0.195~0.37) bulk samples with different compositions were meaured. The refractive index n and extinction coefficient k were obtained. An obvious refractive index enhancement effect was observed in the refractive index spectra for each composition. The energy position of the maximal refractive index value equals approximately that of the band gap. With the decrease of the component, the refractive index increased and the peak position shifted to the low energy direction, which consistented with the absorption edge. The refractive index n at Eg changed linearly with the composition $x$.**

4:40pm **EL+AS+EM-MoA10 Infrared Ellipsometry Study of the Photo-generated Charge Carriers at the (001) and (110) Surfaces of $SrTiO_3$ Crystals and the Interface of Corresponding $LaAlO_3/SrTiO_3$ Heterostructures**, ***Meghdad Yazdi-Rizi***, *P. Marsik, B. Mallett,* University of Fribourg, Switzerland, *K. Sen, A. Cerreta*, University of Fribourg, *A. Dubroka,* Masaryk University, *M. Scigaj, F. Sánchez, G. Herranz*, Institut de Ciència de Materials de Barcelona, *C. Bernhard*, University of Fribourg, Switzerland

With infrared (IR) ellipsometry and DC resistance measurements we investigated the photo-doping at the (001) and (110) surfaces of $SrTiO_3$ (STO) single crystals and at the corresponding interfaces of $LaAlO_3/SrTiO_3$ (LAO/STO) heterostructures. In the bare STO crystals we find that the photo-generated charge carriers, which accumulate near the (001) surface, have a similar depth profile and sheet carrier concentration as the confined electrons that were previously observed in LAO/STO (001) heterostructures. A large fraction of these photo-generated charge carriers persist at low temperature at the STO (001) surface even after the UV light has been switched off again. These persistent charge carriers seem to originate from oxygen vacancies that are trapped at the structural domain boundaries which develop below the so-called antiferrodistortive transition at $T^*$ = 105 K. This is most evident from a corresponding photo-doping study of the DC transport in STO (110) crystals for which the concentration of these domain boundaries can be modified by applying a weak uniaxial stress. The oxygen vacancies and their trapping by defects are also the source of the electrons that are confined to the interface of LAO/STO (110) heterostructures which likely do not have a polar discontinuity as in LAO/STO (001). In the former, the trapping and clustering of the oxygen vacancies also has a strong influence on the anisotropy of the charge carrier mobility. We show that this anisotropy can be readily varied and even inverted by various means, such as a gentle thermal treatment, UV irradiation, or even a weak uniaxial stress. Our experiments suggest that extended defects, which develop over long time periods (of weeks to months), can strongly influence the response of the confined charge carriers at the LAO/STO (110) interface.

## Electronic Materials and Photonics Division
## Room: 14 - Session EM-MoA

## Novel Materials and Devices for Electronics

**Moderators:** Shalini Gupta, Northrop Grumman ES, Rehan Kapadia, University of Southern California

1:40pm **EM-MoA1 2D Materials for Advanced Devices: Integration Challenges and Opportunities**, ***Robert M. Wallace***, University of Texas at Dallas **INVITED**

The size reduction and economics of integrated circuits, captured since the 1960's in the form of Moore's Law, continues to be challenged. Challenges include addressing aspects associated with truly atomic dimensions, while the cost of manufacturing is increasing such that only 3 or 4 companies can afford leading edge capabilities. To address some of the materials physical limitations, "2D materials" such as graphene, phosphorene, h-BN, and transition metal dichalcogenides have captured the imagination of the electronics research community for advanced applications in nanoelectronics and optoelectronics. Among 2D materials "beyond graphene," some exhibit semiconducting behavior, such as transition-metal dichalcogenides (TMDs), and present useful bandgap properties for applications even at the single atomic layer level. Examples include "$MX_2$", where M = Mo, W, Sn, Hf, Zr and X = S, Se and Te

Integration of these materials with semiconductor industrial fabrication processes presents a number of challenges. For example, several synthesis methods have been employed to study 2D material thin film properties including mechanical/liquid exfoliation, chemical bath deposition, vapor phase deposition, and molecular beam epitaxy (MBE). From a manufacturability and cost perspective, vapor phase (including chemical and atomic layer) deposition are the subject of intense research activity in the electronics industry, while MBE methods facilitate the research of large thin films in advance of precursor development for CVD and ALD.

This presentation will examine the state-of-the-art of these materials in view of our research on 2D semiconductors, and the challenges and opportunities they present for electronic and optoelectronic applications. [1]

This work is supported in part by: (i) the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, (ii) the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA, (iii) the US/Ireland R&D Partnership (UNITE) under the NSF award ECCS-1407765, and (iv) the Erik Jonsson Distinguished Chair in the Erik Jonson School of Engineering and Computer Science at the University of Texas at Dallas.

1. S. J. McDonnell and R.M.Wallace, "Critical Review: Atomically-Thin Layered Films for Device Applications based upon 2D TMDC Materials", Thin Solid Films, 616, 482-501 (2016).

3:00pm **EM-MoA5 Enhancement-mode AlGaN/GaN HEMTs Enabled by ALD ZrO2 Gate Dielectrics**, ***Charles Eddy, Jr.****, V.D. Wheeler,* U.S. Naval Research Laboratory, *D.I. Shahin,* University of Maryland, *T.J. Anderson, M.J. Tadjer, A.D. Koehler, K.D. Hobart,* U.S. Naval Research Laboratory, *A. Christou,* University of Maryland, *F.J. Kub*, U.S. Naval Research Laboratory

If power switches based on gallium nitride (GaN) transistors are to achieve widespread adoption, then reliable enhancement-mode (normally-off) operation must be demonstrated. The most advanced GaN transistor, the high electron mobility transistor (HEMT), is naturally a depletion-mode (normally-on) device and is finding rapid adoption in RF applications requiring high power and efficiency. To extend these performance benefits to power switches requires fully depleting the two-dimensional electron gas below the gate in absence of a gate bias. This is often achieved by recess etching the AlGaN barrier under the gate. However, to ensure low gate leakage in such a device further requires a reliable gate dielectric on this recessed surface. Here we report on the development and application of ALD deposited $ZrO_2$ gate dielectrics on recessed etched GaN surfaces. First, a thorough investigation of recessed surface pretreatments is conducted. Then, ALD is used to deposit $ZrO_2$ dielectrics on these surfaces using two precursors – zirconium (IV) tertbutoxide and tetrakis(dimethylamino)zirconium. Through careful variations in ALD growth conditions and precursor selection, we demonstrate the ability to achieve a record positive shift in the threshold voltage for a HEMT of up to +3.99V [1] and low gate leakage currents (5 orders of magnitude lower than reference HEMTs) under on-state conditions (Vgs= +10V and Vds= +20V). These promising early results have been followed by studies of traps in these device structures using a previously established method [2]. Details of recessed surface preparation and trap behavior will be presented.

[1] T.J. Anderson et al., Appl. Phys. Express 9, 071003 (2016).

[2] J. Joh and J. A. del Alamo, IEEE Trans. Electron. Dev. 58, 132 (2011).

3:20pm **EM-MoA6 Interface Engineering with $Al_2O_3$-$HfO_2$ Nanolaminate Gate oxides on Silicon Germanium**, ***Mahmut Kavrik***, University of California at San Diego, *K. Tang,* Stanford University, *E. Thomson, J. Cheng, A.C. Kummel*, University of California at San Diego

Silicon Germanium (SiGe) alloys are promising alternative for silicon in semiconductor industry due to their tunable bandgap and carrier mobility through variation in composition. However, replacement of Si with SiGe requires a new class of high-k dielectric gate oxides with low leakage current for CMOS processing. Germanium content in semiconductor induces new interface defects due to its bonding with oxygen; GeOx is soluble in water and also can out diffuse into the gate oxide. $Al_2O_3$ and $HfO_2$ oxides were incorporated into nanolaminate stacks on the SiGe by Atomic Layer Deposition (ALD). $Al_2O_3$ was deposited with organic precursor trimethylaluminum (TMA) and $H_2O$ on SiGe at 250C after HF and sulfur surface treatments. Sulfur treatment forms Ge-S and Ge-S-Ge bonds and prevents GeOx formation. Subsequently, HfO2 oxide layers were grown with organic precursor Tetrakis(dimethylamido) hafnium(TDMAH) and $H_2O$ at 250C. $Al_2O_3$-$HfO_2$ nanolaminates were terminated with one layer of $Al_2O_3$ to protect oxide from gate metal damage. MOSCAP studies showed low Dit with hig Cox with Nanolaminate structure.

4:00pm **EM-MoA8 Encapsulation of AlGaN/GaN High Electron Mobility Transistor based Hydrogen Sensor for Humid Ambient Sensing Application**, *S. Jung, H. Kim,* Dankook University, *K.H. Baik,* Hongik University, *F. Ren, S.J. Pearton,* University of Florida, ***Soohwan Jang***, Dankook University

Hydrogen is environmentally friendly alternative energy source and carrier for automotive and fuel cell applications as well as in many industrial processes. Hydrogen gas is colorless, odorless, extremely reactive with oxygen, and has very low ignition energy. Especially, leaking gas from pressurized container may elevate its temperature, and induce spontaneous flammable ignition due to its negative Joule-Thomson coefficient. Therefore, hydrogen gas sensing systems are essential in various hydrogen related applications. GaN based material system is well-suited to hydrogen sensing because of its wide bandgap for high temperature operation, and mechanical and chemical robustness for device reliability. Many types of devices based on the GaN, including Schottky diodes, metal oxide semiconductor diodes, GaN nanowires and AlGaN/GaN high electron mobility transistors have been developed for fast and sensitive detection of hydrogen. Among them, AlGaN/GaN HEMTs with a 2 dimensional electron gas (2DEG) channel induced by piezoelectric and spontaneous polarization between the AlGaN and GaN layers showed high sensitivity to change in surface charge created by catalytic reaction of Pt or Pd with hydrogen. With 30 % Al concentration in AlGaN layer, 5~10 times higher electron densities in 2DEG are obtained compared to typical GaAs or InP HEMTs, which induces higher current and better sensitivity of the device. However, one of issues with semiconductor based hydrogen sensors is the fact that their sensitivity is significantly degraded in the presence of humidity or water. Water molecules block the catalytically active sites of sensing material, and results in the significant reduction in hydrogen detection signal. By employing encapsulation layer which prevents water molecules from adsorbing on the active sites of the sensor while selectively allowing penetration of hydrogen molecules, this issue can be solved. In this paper, we demonstrate that the device encapsulated with a moisture barrier does not suffer from any significant change in hydrogen detection sensitivity in the presence of moisture and that the devices can be repeatedly cycled to temperatures up to 300°C without any change in characteristics. Also, the device did not respond to the other gases including $CH_4$, CO, $NO_2$, $CO_2$, and $O_2$.

4:20pm **EM-MoA9 Work Function Measurements of Metal Gate - TiAlC by Ultraviolet Photoelectron Spectroscopy**, ***Yibin Zhang****, H. Wang, D. Shao, Y. Liang*, GlobalFoundries Inc

In order to obtain high performance and low power in integrated circuits (IC), feature sizes continue to shrink and new materials are being developed. One major challenge is finding a metal gate electrode with the appropriate work function when paired with a gate oxide. Titanium-Aluminum-Carbide (TiAlC) films deposited by Atomic Layer Deposition (ALD) were introduced in the semiconductor industry in the 22nm and beyond FINFET technology node. TiAlC can provide the necessary work function and ALD offers better thickness control, uniformity and conformity compared to Plasma Vapor Deposition (PVD). Electrical measurements are typically used to measure a film's work function. However, in an IC manufacturing environment this type of measurements can be performed only after several processing steps following the TiAlC deposition. It is often difficult and not cost effective to "rework" the affected wafers resulting in the loss of both product and time. Thus, it is important to monitor the work function during manufacturing. X-ray Photoelectron Spectroscopy (XPS) is used for in-line monitoring of the film composition and thickness, but it cannot directly measure the work function of TiAlC. In this work we demonstrate that Ultraviolet Photoelectron Spectroscopy (UPS) can provide work function measurements directly after the film deposition, to more effectively control the TiAlC ALD process parameters and resulting film properties. In addition, X-ray reflectivity (XRR) and X-ray diffraction (XRD) were used to investigate TiAlC film's density and crystallinity.

4:40pm **EM-MoA10 Nitride Based Avalanche Photodiode Detector Structures for Nuclear Detection Applications**, ***Vincent Woods****, L. Hubbard, L. Campbell,* Pacific Northwest National Laboratory, *N. Dietz,* Georgia State University, *Z. Sitar*, North Carolina State University **INVITED**

Group III-N avalanche photodiodes (APD) offer tailorable UV sensitivity and selectivity not currently available for scintillated light detectors. Materials growth challenges continue to hamper the development and implementation of UV III-N detectors. This presentation details the efforts at Pacific Northwest National Laboratory in collaboration with North Carolina State University and Georgia State University to develop device structures and fabrication processes Group III-N APDs. The focus of these efforts is to produce nitride photomultiplier (NPM) devices similar to a silicon photomultiplier (SiPM). Compared to traditional photomultiplier tubes (PMTs), the NPMs can be smaller, more rugged, consume less power than PMTs, and have lower dark currents than SiPMs for UV light detection.

The large bandgap of III-N systems allows for UV photo-detection that is solar blind resistant to ambient stray light. Unlike silicon, the bandgap and associated dark current in the III-N system can be tuned by changing the composition of the $Al_xGa_{1-x}N$ materials system. A direct advantage of the III-N APDs over SiPMs and PMTs is the matching of the device (by matching the band gap) to a scintillator.

Conventional radiation detection relies on the use of dyes to wavelength shift the scintillated light to match the PMT or SiPM. Tailoring the APD to the scintillator allows for increased resolution of scintillated light without broadening/attenuation from dye interactions. A tailorable APD also allows for exploration of scintillating materials which cannot be dye matched to a SiPM or PMT. The tailorable III-N system opens up new avenues in radiation detection. Research into the selection of appropriate scintillator materials and compositional requirements of the Nitride-based APD structures will be presented. In addition to the materials characterization, optoelectronic modeling aimed towards efficient APD operation will be shown.

The progress in the growth of nitride heterostructures in both Al-rich and Ga-rich AlGaN materials systems will be presented along with detailed materials characterization. This project is developing the materials capability to tailor III-N APDs to match scintillated light. The development of materials knowledge and capability will enable tailorable III-N APDs for direct matching to UV scintillated light, a significant improvement over current technology.

## 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.

[1] B. Göhler V. Hamelbeck, T. Z. Markus, M. Kettner, G. F. Hanne, Z. Vager, R. Naaman, and H. Zacharias, Science **331**, 894 (2011).

[2] M. Á. Niño, I. A. Kowalik, F. J. Luque, D. Arvanitis, R. Miranda, and J. J. de Miguel, Adv. Mater. **26**, 7474 (2014).

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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[2] I. M. Miron Nat. Mat 9 pp230 (2010)

[3] I. E. Dzyaloshinskii , J. Exp. Theor. Phys. 5, pp1259 (2007),; T. Moriya , Phys. Rev. 120 , pp91 (1960).

[4] G. Chen, et al., Ap. Phys. Lett. 106, 062402 (2015)

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.

[1] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, D. M. Treger; *Science* **294** 1488 (2001).

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[3] O. Ben Dor, S. Yochelis, S. P. Mathew, R. Naaman, and Y. Paltiel *Nature Communications* **4**, 2256 (2013).

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[5] O. Ben Dor, N. Morali, S. Yochelis, and Y. Paltiel; *Nano letters* 14 6042 (2014).

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7] O. Koslovsky, S. Yochelis, N. Livneh, M. Harats, R. Rapaport, and Y. Paltiel, *Journal of Nanomaterials* 938495 **2012** (2012).

[8] H. Alpern, E. Katzir, S. Yochelis, Y. Paltiel, and O. Millo; New J. Phys. 18 113048 (2016).

[9] O. Ben Dor, S. Yochelis, A. Radko, K. Vankayala, E. Capua, A. Capua, S.-H. Yang, L. T. Baczewski, S. S. P. Parkin, R. Naaman, and Y. Paltiel; *Nature Communications*, **8** 14567 (2017).

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 $1\times10^6$ A·cm$^{-2}$, or about $1\times10^{25}$ electrons·sec$^{-1}$·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.

## MEMS and NEMS Group
## Room: 24 - Session MN+EM+NS-MoA

## Nano Optomechanical Systems/Multiscale Nanomanufacturing

**Moderators:** Robert Ilic, NIST, Meredith Metzler, University of Pennsylvania

1:40pm **MN+EM+NS-MoA1 GHz Integrated Acousto-Optics**, ***Mo Li***, University of Minnesota **INVITED**

Integrating nanoscale electromechanical transducers and nanophotonic devices potentially can enable new acousto-optic devices to reach unprecedented high frequencies and modulation efficiency. We demonstrate acousto-optic modulation of a photonic crystal nanocavity using acoustic waves with frequency up to 20 GHz, reaching the microwave K band. Both the acoustic and photonic devices are fabricated in piezoelectric aluminum nitride thin films. Excitation of acoustic waves is achieved with interdigital transducers with periods as small as 300 nm. Confining both acoustic wave and optical wave within the thickness of the membrane leads to improved acousto-optic modulation efficiency in the new devices than that obtained in the previous surface acoustic wave devices. In a photon-phonon waveguide, we further demonstrate strong Brillouin scattering of light by electromechanically excited acoustic waves. Our system demonstrates a novel scalable optomechanical platform where strong acousto-optic coupling between cavity-confined or guided photons and high frequency traveling phonons can be explored.

2:20pm **MN+EM+NS-MoA3 Coupling Piezoelectric MEMS to Cavity Optomechanics**, ***Kartik Srinivasan***, NIST **INVITED**

Establishing a link between the radio frequency (RF) and optical domains is a topic of relevance to a variety of applications in communications, metrology, and photonic quantum information science. Acoustic wave devices represent an opportunity to mediate such transduction in a chip-integrated format. The approach we are pursuing uses materials that are both piezoelectric, to couple RF waves to strain fields, and photoelastic, to couple strain fields to optical waves.

One architecture that we have recently explored is based on exploiting these effects in GaAs. First, interdigitated transducers (IDTs) convert 2.4 GHz RF photons into 2.4 GHz propagating surface acoustic waves. These acoustic waves are routed through phononic crystal waveguides and are coupled to a nanobeam optomechanical cavity that supports both a highly localized 2.4 GHz breathing mechanical mode and a high quality factor 1550 nm optical mode. In contrast to non-resonant excitation of photonic structures with IDTs, here the phononic waveguide preferentially excites a localized mechanical mode, which in turn strongly interacts with the optical mode through the photoelastic effect. Finally, the optical mode can be out-coupled or excited via an optical fiber taper waveguide. Using this platform, we demonstrate preparation of the breathing mode in a coherent state at any location in phase space, and optically read out an average coherent intracavity phonon number as small as one-twentieth of a phonon. In the time-domain, we show that RF pulses are mapped to optical pulses, forming a resonant acousto-optic modulator with a sub-Volt half-wave voltage. We also observe a novel acoustic wave interference effect in which RF-driven motion is completely cancelled by optically-driven motion, enabling the demonstration of interferometric opto-acoustic modulation in which acoustic wave propagation is gated by optical pulses.

While the above platform has been shown to provide a coherent interface between the RF, optical, and acoustic domains, the overall efficiency is limited by imperfect matching across the various interfaces, e.g., IDT-to-phononic crystal waveguide, etc. In the final part of my talk, I will outline efforts to improve upon the transduction efficiency of the system.

3:00pm **MN+EM+NS-MoA5 Collective Nano-optomechanics for Sensing Applications**, ***Eduardo Gil Santos**, W. Hease,* Universite Paris Diderot, France, *A. Lemaitre,* Centre de Nanosciences et Nanotechnologies, France, *M. Labousse, C. Ciuti, G. Leo, I. Favero*, Universite Paris Diderot, France

Optomechanical resonators have been the subject of extensive research in a variety of fields, such as sensing, communication and quantum technologies. Our recent investigations on the capabilities of optomechanical semiconductor disk resonators to operate as sensors in liquids have revealed an astonishing potential. Minimum mass detection of $14\cdot10^{-24}$ g, density changes of $2\cdot10^{-7}$ kg/m$^3$ and viscosity changes of $5\cdot10^{-9}$ Pa·s, for 1s integration time, are extrapolated from our measurements in liquids.

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* **Falicov Student Award Finalist**

After landmark experiments realized on single resonators, the use of multiple optomechanical cavities is essential to further improve their sensing capabilities, as it enlarges the sensing area while keeping their individual assets. This evolution towards collective nano-optomechanics hence bears potential for a variety of sensing applications, but for quantum or topological photonics as well. Unfortunately, the collective configurations are usually impeded by the residual disorder imposed by nanofabrication techniques, which naturally detunes high optical Q resonators and precludes resonant interactions between them. Therefore, overcoming fabrication imperfections and allowing spectral alignment of resonators is essential.

Here, we develop a new simple and scalable post-fabrication method to achieve such alignment in a permanent manner. The method introduces an approach of cavity-enhanced photoelectrochemical (PEC) etching in a fluid (gas or liquid). This resonant process is highly selective and allows controlling the resonator size with sub-pm precision, well below the material's interatomic distance. Light resonantly injected into the optical mode of an optical resonator immersed in a fluid triggers an etching process, leading to a fine-tuning of the resonator's dimensions. The evolution of dimensions is monitored continuously by tracking the resonator's optical resonance with a laser. This tuning process is naturally scalable to multiple resonators. We demonstrate it using a cascaded configuration where optomechanical disk resonators, each supporting its own localized optical and mechanical mode, are unidirectionally coupled through a common optical waveguide. The technique is illustrated by finely aligning up to five resonators in liquid and two in air, opening the way of fabricating large networks of identical resonators.

As an example of application of this tuning technique, we explore the resonant optical interaction of multiple nano-optomechanical systems. We observe a first form of collective behavior involving several distant resonators, where a unidirectional flow of light frequency-locks a chain of nano-optomechanical oscillators.

### 3:20pm **MN+EM+NS-MoA6 Microporous Nanophotonic Mechanical Cantilevers for Mass Sensing**

*Anandram Venkatasubramanian*, *V.T.K. Sauer*, *J.N. Westwood-Bachman*, University of Alberta and The National Institute for Nanotechnology, Canada, *K. Cui*, *S.K. Roy*, *M. Xia*, National Institute for Nanotechnology, National Research Council, Canada, *D. Wishart*, University of Alberta, Canada, *W.K. Hiebert*, University of Alberta and The National Institute for Nanotechnology, Canada

The Gas chromatography (GC) – Mass spectrometry (MS) system is the industry benchmark in chemical analysis. However the large size of the Mass spectrometry unit makes it unsuitable for portable applications. Hence a portable universal mass sensing device that can be used with portable GCs needs to be developed. In this regard, recent demonstration with nano opto-mechanical system (NOMS) devices in conjunction with a GC system have proven that these kinds of sensors have the breakthrough potential to improve the sensitivity of portable GCs. Those demonstrations using NOMS devices have shown these sensors to match the mass detection limits of nanoelectromechanical systems (NEMS) sensors and can potentially better their performance owing to their superior displacement sensitivity compared to NEMS.

In this regard, a free space interferometry system based nanophotonic sensor was developed and attached to a conventional GC. The nanophotonic sensor consists of a microring racetrack resonator (for concentration sensing) with a nanomechanical beam (for mass sensing) adjacent to it. Common method to improve the sensitivity of a nanomechanical beam is to apply surface coatings. However, the application of surface coatings can potentially affect its universal sensing characteristics. Hence an alternate way to improve the adsorption sensitivity is to increase the surface area of the nanomechanical sensor to aid in increasing the number of gas adsorption sites.

In this paper we increase the surface porosity of nanomechanical beam by stain etching. Care was taken to protect the adjacent microring resonator from stain etching as surface pores can negatively affect the performance of the ring resonator due to increased scattering. The stain etching was conducted using vanadium oxide/Hydrofluoric acid based chemistry to etch ~ 10nm pores of random morphology on the surface. Based on an estimated porosity of <15% by volume, we have noted an increase in mass adsorption of ≥ 50 - 100% when tests were conducted using different volatile organic compounds. In other words, a mass adsorption enhancement factor of 1.5 to 2 has been achieved. Due to this enhanced adsorption, the mass detection threshold has improved by an order of magnitude (~$10^{-19}$ g). To the best knowledge of the authors, this is the first time NOMS based porous nanomechanical mass sensor has been developed.

Mass Adsorption Enhancement Factor = Adsorption frequency shift for porous beam/Adsorption frequency shift for non porous beam

### 4:00pm **MN+EM+NS-MoA8 Tunable Resistivity in Inkjet Printed Circuit by Plasma Reduction of Particle-free, Stabilizer-free Ink**

*Y. Sui*, *S. Ghosh*, *C. Miller*, *R.M. Sankaran*, ***Christian Zorman***, Case Western Reserve University

Inkjet printing offers a low-cost, rapid methodology to produce patterned metal thin films on flexible substrates. The most commonly used ink consists of colloidal suspensions of nanoparticles prepared by wet chemical reduction of metal salts. Even after concentrating the nanoparticles through solution processing, the as-printed ink usually exhibits a low conductivity due to the presence of organic molecules that help stabilize the nanoparticles from agglomeration and precipitation. High temperature (>200 C) treatment is then required after printing to remove the insulating organics and sinter the nanoparticles. The thermal step can limit printing on polymers such as PDMS, paper, and 3D printed polymers.

Here, we present a particle-free, stabilizer-free ink and a low-temperature plasma reduction process to produce electrically conductive metallic patterns on temperature-sensitive without any additional thermal step. The ink is comprised of a metal salt, a solvent, and a viscosity modifier, and is absent of any large organic molecules that cannot be evaporated after printing. The as-printed and dried metal salt is then treated with a plasma formed in a low-pressure argon environment. Even without the presence of highly reactive atomic and molecular hydrogen, this process is found to be sufficient to reduce the metal salt to highly conductive metal with resistivities approaching bulk values. More importantly, we found the resistivity of the printed structure can be tuned over a range of 2 orders of magnitude by varying the plasma power and treatment time. Thus far, we have demonstrated this general approach for silver (Ag) and tin (Sn) from silver nitrate (AgNO3) and tin (II) chloride (SnCl2), respectively. Details of the material properties as assessed by materials characterization and electrical conductivity measurements, device application to RC filter circuits, and applicability to other metals will also be discussed.

### 4:20pm **MN+EM+NS-MoA9 Cold Forming of Shallow Spherical Micro Caps by Nano Imprinting**

***Asaf Asher***, *E. Benjamin*, *L. Medina*, *S. Lulinsky*, Tel Aviv University, Israel, *R. Gilat*, Ariel University, Israel, *S. Krylov*, Tel Aviv University, Israel

Many nonlinear systems are distinguished by bistability, which manifests itself as the coexistence of two equilibria under the same loading. Progress in the development of micro and nano structures stimulated renewed interest in the mechanics of bistable elements. Applications of these devices in the realm of micro and nanoelectromechanical systems (MEMS/NEMS) include switches, sensors, non-volatile memories, micro-pumps, micro-resonators and deformable mirrors. While curved beam-type bistable micro structures were intensively investigated both theoretically and experimentally much less attention was paid to two-dimensional bistable structures such as initially curved plates and shells (caps). One of the reasons is that lithography-based processes commonly used in MEMS/NEMS are essentially planar and are not suitable for fabrication of cap-like structures with an out-of-plane curvature. Existing approaches include gray-scale lithography or a glass blowing technique.

In this work we discuss several approaches for fabrication of shallow micro shells. One of the directions is the use of the cold forming techniques, when stamping changes a flat thin foil of ductile material into double-curvature components. While multiple variations of this process were used at the macro scale, much less works reported the implementation of this technique in MEMS. In the framework of the fabrication process used in our work, a layer of Al or Cu is deposited on top of a Si wafer. Sputtering is implemented for the creation of a thin seed layer, followed by electrodeposition used to increase the layer thickness to a desired value. Next, an opening is etched through the wafer using deep reactive ion etching (DRIE). Finally, the forming process is performed using nano-imprinting lithography tool. The tool allows very precise control of the force applied to the structure as well as the stamp temperature, displacements and rate of loading. Finite elements analysis and compact reduced order models are used for the evaluation of the desired parameters. Prior to forming, residual stress of the thin suspended membranes is estimated using a resonance method, by means of comparison of the measured natural frequencies of the device with the model predictions. We discuss suitability of different structural materials, deposition methods and stamping techniques for the formation of non-planar three-dimensional micro structures.

### 4:40pm **MN+EM+NS-MoA10 Plate Mechanical Metamaterials: The Thinnest Plates You Can Pick Up by Hand**

***Igor Bargatin***, University of Pennsylvania **INVITED**

Recently, my group has demonstrated a new class of ultra-lightweight plate-shaped mechanical metamaterials, which we named "plate mechanical metamaterials". Using a periodic three-dimensional patterning, we fabricated free-standing plates up to 1 cm in size out of aluminum oxide (alumina) films as thin as 25 nm. Weighing as little as 0.1 gram per square meter, they are among the thinnest and lightest freestanding solids that can be handled with bare hands. We also combined multiple ultrathin layers of alumina to create a nanoscale analog of paper-based corrugated cardboard. Unlike cardboard, these plates have the ability to "pop back" to their original shape, without damage, even after undergoing multiple sharp bends by more than 90 degrees.

Like the nanotruss -based mechanical metamaterials reported by other groups, plate mechanical metamaterials are extremely lightweight and resilient due to their nanoscale thickness and microscale cellular structure. However, in contrast to the cube-shaped metamaterials that typically form a lattice easily penetrated by the ambient air, our plates form flat continuous plates. Ultralow weight, mechanical robustness, thermal insulation, as well as chemical and thermal stability of alumina make plate metamaterials attractive for numerous applications, including structural elements in flying microrobots, high-temperature thermal insulation in energy converters, testing of nanoscale strength enhancement, new types of optical and acoustic metamaterials, as well as ultrathin MEMS/NEMS sensors and ultra-lightweight hollow MEMS/NEMS resonators.

## Nanometer-scale Science and Technology Division
## Room: 19 - Session NS+HC+SS-MoA

## Oxides in Nanotechnology
### **Moderator:** Nancy Burnham, Worcester Polytechnic Institute

2:00pm **NS+HC+SS-MoA2 Epitaxial Growth and Characterization of WO3 and WO$_{3-\delta}$ Thin Films**, ***Yingge Du***, *Z. Yang, Z.H. Zhu, C. Wang*, Pacific Northwest National Laboratory

Tungsten trioxide ($WO_3$) based thin-film materials are of significant importance because of their diverse structures and wide range of properties. These materials have found widespread applications in display devices, electrochromic "smart" windows, gas sensors, catalysis, and photocatalysis. Investigations of $WO_3$ films in epitaxial form offer definite advantages over porous or polycrystalline forms for fundamental science studies. For example, the ability to detect and eliminate secondary phases and surfaces simplifies the material system and makes it easier to establish defensible cause-and-effect relationships. While amorphous, polycrystalline, and epitaxial $WO_3$ films have been prepared by several methods such as evaporation of $WO_3$, sputtering, and pulsed laser deposition, the growth of epitaxial $WO_3$ films by molecular beam epitaxy (MBE) is much less explored.

We examined three different ways to grow epitaxial $WO_3$ films by MBE – by evaporating WO3 powders from an effusion cell, by evaporating $WO_x$ surface layers formed on W metal surface, and by evaporating tungsten metal in an oxidizing environment. Epitaxial films are formed in all three cases but the growth characteristics vary significantly. The films from the first two methods are found to grow as stoichiometric islands first, while the third method leads to layer by layer growth, with significant amount of ordered oxygen vacancies. The films are characterized *in-situ* by RHEED and XPS, and *ex-situ* by XRD, SIMS, and STEM.

2:20pm **NS+HC+SS-MoA3 Oxide Surfaces: Structure, Adsorption, Growth**, ***Ulrike Diebold***, TU Wien, Austria **INVITED**

Fundamental investigations into the surface properties of oxides have experienced a continued growth. The reasons for this increasing interest are quite clear: after all, most metals are oxidized under ambient conditions, so in many instances it is the oxidized surface that deserves our attention. In addition, metal oxides exhibit an extremely wide variability in their physical and chemical properties. These are exploited in established and emerging technologies such as catalysis, gas sensing, and energy conversion schemes, where surfaces and interfaces play a central role in device functioning. Hence a more complete understanding of metal oxide surfaces is desirable from both fundamental and applied points of view.

By using Scanning Probe Microscopy measurements, in combination with Density Functional Theory calculations and area-averaging spectroscopic techniques, great strides have been made in understanding the atomic-scale properties of the surfaces of these complex materials.

In the talk I will give examples drawn from recent studies on several metal oxide systems, including $TiO_2$, $Fe_3O_4$, $In_2O_3$, $ZrO_2$, and perovskites. I will point out the advantages of directly viewing, and manipulating, point defects and single molecules with atomic precision, and how inspecting central processes such as charge transfer to adsorbates can further a deep mechanistic understanding. I will also discuss new opportunities based on recent technique development such as Scanning Force Microscopy, and the challenges and possible rewards in exploring more complex materials.

3:00pm **NS+HC+SS-MoA5 Imaging and Sensor Applications of infiltrated Zinc Oxide**, ***Leonidas Ocola***, Argonne National Laboratory, *V. Sampathkumar*, University of Chicago, *N. Kasthuri, R.P. Winarski*, Argonne National Laboratory, *Y. Wang, J.H. Chen*, University of Wisconsin - Milwaukee

With the increased portfolio of materials that can be deposited using atomic layer deposition (ALD) there has been an increased interest in infiltrated metal oxides such as zinc oxide for novel applications. We find that ZnO metal oxide ALD infiltration can be useful for nanoscale resolution imaging of biological samples in electron and X-ray microscopy and to fabricate novel UV and gas nanosensors with high sensitivity. The ALD infiltration utilizes similar concepts of the ALD coating process with the significant difference in process exposure times, pressure, and purpose. The purpose is to allow the precursor gases infiltrate a porous media (such as a dry biological sample or a photoresist polymer) and allow the reaction to occur inside the material matrix.

Most biological materials have problems with charging when imaging with electrons and low contrast when imaging with hard X-rays. In this presentation we describe the use of infiltrated ZnO as a means to address both charge dissipation in electron microscopy and contrast enhancement for X-ray microscopy. With ZnO infiltration it is feasible to coat a 2 – 3 nm conductive metal oxide film throughout a porous biological sample, and image both the surface and the interior of a sample without any further sample recoating. We demonstrate this technique can be applied on tooth and brain tissue samples. We show that high resolution X-ray tomography can be performed on biological systems using Zn K edge (1s) absorption to enhance internal structures, and obtained the first nanoscale 10 KeV X-ray absorption images of the interior regions of a tooth.

In terms of device fabrication we use SU8 as a negative resist that allows for localization of the infiltration process. We have used this property to make a device that is UV sensitive, and that is sensitive to ppm concentrations of gases by using infiltrated zinc oxide. The large bandgap and semiconductor properties of ZnO allow for a visible-blind ultra violet light sensor. We used a standard UV flashlight that emits at 408 nm as the UV source. We also tested the same device for sensing gases like nitrous oxide and formaldehyde. We show that the device can detect these gases with concentrations of 5 ppm. The change in current for such low concentrations was measured to be between 25% and 35 %.

- Use of the Center for Nanoscale Materials and the Advanced Photon Source, both Office of Science user facilities, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. Additional funding by IARPA, (ARIADNE) under Contract D16P00002

3:20pm **NS+HC+SS-MoA6 Plasma Modified Gas Sensors: Bridging the Gap Between Tin Oxide Nanomaterials and Paper-Based Devices**, ***Kimberly Hiyoto***, *E.R. Fisher*, Colorado State University

Metal oxide nanomaterials are desirable for solid-state gas sensors because of their low manufacturing cost and ability to detect a wide variety of gases through changes in resistance resulting from gas-surface interactions. The substrates that support these materials, however, are often brittle and their smooth surface limits the amount of nanomaterial that can be exposed to target gases. Recent attempts to address these issues utilize paper substrates, that are not only low cost, but flexible to allow for a more robust device. Moreover, the porous, fibrous morphology of paper substrates provides significantly increased surface area for attaching more nanomaterials when compared to a traditional substrate of the same size. Despite recent improvements to paper-based metal oxide gas sensors, tin(IV) oxide ($SnO_2$) nanomaterials require high operating temperatures, thus have not yet been successfully translated to paper-based sensors. Here, we describe how low power (30 – 60 W) $Ar/O_2$ plasma modification, can be used to enhance gas-surface interactions of $SnO_2$ paper-based sensors while maintaining desirable bulk nanomaterial and substrate architecture. X-ray photoelectron spectroscopy revealed plasma treatment increased adsorbed oxygen, which is thought to improve sensor response by promoting gas-surface interactions. Indeed, plasma modified $SnO_2$ nanomaterials on a paper substrate exhibit improved response to ethanol, carbon monoxide, and benzene at ambient temperature. Furthermore, scanning electron microscopy demonstrates that plasma treatment does not damage the morphology of $SnO_2$ or the paper substrate. Response and recovery studies on these devices will be discussed along with $SnO_2$ nanomaterial gas sensors created on more traditional substrates (e.g. $ZrO_2$) as another measure of sensor performance. A better understanding of how plasma modification and the resulting changes in surface chemistry affect sensor performance is an important step towards achieving improved paper-based gas sensors using $SnO_2$ nanomaterials.

4:00pm **NS+HC+SS-MoA8 Understanding the Initial Stages of Oxidation in Nickel-Chromium Alloys**, *P. Reinke*, ***William H. Blades***, *G. Ramalingam*, University of Virginia

Through a combined experimental and computational effort, the interaction of oxygen with Nickel-Chromium alloys is studied. Prior to the formation of a full oxide layer, the physical and chemical processes behind the initial stages of oxidation are not well understood. This work fills a significant gap in our understanding of binary alloy oxidation. Scanning Tunneling Microscopy and Spectroscopy were used to observe the onset of oxide formation. These surface techniques are combined with Bandgap and Density of States maps, which lend themselves as powerful tools when studying surfaces with heterogeneity at the nanoscale. Ni-Cr(100) thin films with a range of compositions were prepared on MgO(100) in UHV and exposed to controlled amounts of oxygen up to 400L. Previous experiments have shown chromia to be the dominant oxide when Ni-Cr alloys are oxidized with a partial pressure of $p(O_2)<10^{-7}$mbar at 300ºC. Under these oxidation conditions the Ni prefers the kinetically favorable Ni(100)-c(2x2)-O reconstruction. Our experiments demonstrate that a combination of increased chromium concentration, which locally catalyzes the Ni, and an elevated oxidation temperature of 500ºC can overcome the activation barrier for NiO formation. The statistical analysis of island densities and sticking coefficient, in direct comparison of Ni and Ni-Cr surfaces, support the idea that NiO nucleation is facilitated by the presence of Cr. Early oxidation steps reveal that initial NiO nucleation and growth occurs along the step edges of the Ni-Cr alloy. This is in contrast to Ni(100)-c(2x2)-O where the step edges are passivated and devoid of reactive kink sites. We suggest that the presence of Cr at the step edges lowers the activation barrier and thus promotes rapid NiO formation. Anneal periods have shown that at low coverage, the NiO is readily desorbed from the surface leaving behind small oxides particles and regions with chemisorbed oxygen. Further oxidation steps create a high quality crystalline oxide layer, which is significantly more stable at elevated temperatures. Density Functional Theory is used to develop an understanding of the electronic and geometric structure of the oxidized Ni-Cr alloys and the effect of chromium on the local bonding environment. This collective experimental and theoretical approach has offered greater insight into alloy-oxide interface structure, and the role of transition metal dopants in the oxidation process in the pre Cabrera-Mott regime. This work is supported by the Office of Navel Research MURI “Understanding Corrosion in Four Dimensions,” Grant N00014-14-1-0675.

4:20pm **NS+HC+SS-MoA9 Evaluation of Titanium Doped β-$Ga_2O_3$ Thin Films in Extreme Environment for Application in Oxygen Sensors**, ***Sandeep Manandhar***, *A.K. Battu*, *C.V. Ramana*, University of Texas at El Paso

The reliable and efficient operation of power generation systems has become one of the grand challenges of today’s research in order to meet the ever-increasing demand for energy and sustainability. The improvement in power/energy generation processes, in particular, for those depend on fossil fuels, the higher temperature and accurate measurement of the combustion environment and the emissions produced by the combustion via proper selection of sensing materials can enhance the efficiency and reliability. While several candidate metal oxides ($SnO_2$, ZnO, $TiO_2$, $WO_3$, and $Ga_2O_3$) exhibit high sensitivity chemical gases, β-$Ga_2O_3$ has shown to function as oxygen sensor at high temperatures (>700°C). However, the response time and sensitivity must be improved in order to utilize them in practical applications. While improved sensor characteristics are seen in various metal/ion doped β-$Ga_2O_3$, fundamental understanding of the long term effects of high temperature exposure on the structure and properties of doped β-$Ga_2O_3$ films is missing at this time. However, such studies are quite important to predict the thermodynamic stability and performance in extreme environments. In this work, we performed a detailed study to understand the effect of extreme environment on titanium (Ti) doped β-$Ga_2O_3$. The real environment condition for sensor (>700°C) application were simulated to understand the effect of temperature on the crystal structure, mechanical properties, electronic properties and oxidation states of Ti doped β-$Ga_2O_3$. The results will be presented and compared with as prepared Ti doped β-$Ga_2O_3$ films in the context of utilizing these materials in oxygen sensor applications.

4:40pm **NS+HC+SS-MoA10 Characterization of Infiltrated ZnO in PS-b-PMMA Nanostructures**, ***Paris Blaisdell-Pijuan***, University of Chicago, *L.E. Ocola*, Argonne National Laboratory

We have characterized the growth of ZnO using sequential infiltration synthesis (SiS) on PS-b-PMMA block copolymers (BCP) of spherical and cylindrical sub-20nm morphologies and studied how the photoluminescence of these nanostructures varies per its seed layer. Investigation of these structures was done using atomic force microscopy (AFM), spectrofluorometry, Raman spectroscopy, and scanning electron microscopy (SEM). We report blue-shifted photoemission at 335nm (3.70eV), suggesting quantum confinement effects. Samples of ZnO prepared with an alumina seed layer showed additional defect state photoemission at 470nm and 520nm for spherical and cylindrical BCP morphologies, respectively. Defect photoemission was not observed in samples prepared without a seed layer. No Raman peaks were observed for any samples with less than four cycles of ZnO, implying the absence of phonons and the functionality of these ZnO nanostructures as isolated emitters. Rapid thermal annealing of samples in air above 500 ºC began to coalesce and show photoemission characteristic of bulk ZnO at 370nm (3.35eV). Our work demonstrates that ZnO nanostructures grown on PS-b-PMMA via SiS are advantageous in uniformity and size, and exhibit unique fluorescence properties. These observations suggest that infiltrated ZnO in PS-b-PMMA nanostructures lends itself to a new regime of applications in photonics and quantum materials.

## Plasma Processing for Biomedical Applications Focus Topic
## Room: 12 - Session PB+BI+PS-MoA

### Plasma Agriculture & Processing of Biomaterials
**Moderator:** Kristian Wende, INP Greifswald

1:40pm **PB+BI+PS-MoA1 Control for Plant Disease and Development by Atmospheric Pressure Plasma**, ***Gyungsoon Park***, Kwangwoon University, Republic of Korea **INVITED**

Previously, we observed that seeds contaminated with *Fusarium fujikuroi* (a fungus causing rice bakanae disease) were more effectively disinfected in water by arc discharge plasma than ozone. Efficiency of disinfection was decreased when the distance between seeds and electrodes becomes greater. This indicates that shockwave from arc plasma may play an important role in seed sterilization, and we measured about 50-60 atm shockwave pressure. In addition, seed surface became more hydrophillic after plasma than ozone treatment indicating that water containing ROS and RNS can more easily get inside hull. Ozone level in water was decreased when seeds were present. This is probably due to the chemical reaction of ozone with seed surface molecules and will eventually cause the decrease in efficiency of seed disinfection. We also analyzed the effect of water and buffer treated with microwave plasma generated gas containing nitric oxide (PGNO) on development of spinach. The real time level of nitric oxide in water and phosphate buffer was increased to about 100 µM after treatment with PGNO for 50 min. Spinach treated with PGNO water seems to become more tolerant to drought stress. Our work was supported by the National Research Foundation of Korea (NRF) grant (No. 2010-0027963), Rural Development Administration (RDA) grant (No. PJ009891) and National Fusion Research Institute (NFRI) grant.

2:20pm **PB+BI+PS-MoA3 Biomass Pyrolysis Using Low Temperature Plasma**, *Y. Gao*, *N.B. Uner*, *J. Meyer*, *M. Foston*, ***Elijah Thimsen***, Washington University in St. Louis

Low temperature plasmas (LTP) are recently being used for processes involving complicated heterogeneous chemistry. Due to their unique non-equilibrium environment and the abundance of reactive radicals, LTPs are expected to bring selectivities and reactivities that are difficult to obtain in systems governed by local thermal equilibrium. In this study, we utilize low temperature plasmas for converting biomass into more valuable chemicals.

Biomass is an abundant and renewable source of carbon. It is recently reported that biomass can be supplied and processed at a scale large enough that is comparable to petroleum [1]. Current research efforts are focused on upgrading biomass into hydrocarbons and valuable aromatic compounds. One common method is to pyrolyze biomass into oils at high pressure. However, the product distribution usually turns out to be very broad, therefore the yields of the desired components are often low. Another common method is to gasify the biomass into syngas, a mixture of CO and $H_2$. Both pyrolysis and gasification are indirect routes of converting biomass into valuable chemicals. Complicated additional steps are usually required, as in the case of hydrodeoxygenation of pyrolysis oil or production of various paraffins/olefins via Fischer-Tropsch synthesis from biomass-derived syngas. Furthermore, a common drawback for both pyrolysis and gasification methods is the deactivation of catalysts due to coke formation.

In this study, we demonstrate a single-step process without catalysts that generates oxygen-free hydrocarbons with high yield. We will report low temperature plasma conversion of lignocellulosic biomass in a gram-scale radio frequency reactor. Preliminary work shows that the plasma rapidly converts solid feedstock into primarily small chain hydrocarbons. Effects of process parameters such as plasma power, plasma gas composition, operating pressure and biomass feedstock will be presented, along with a techno-economic analysis of the process.

[1] U.S. Department of Energy, “2016 Billion-Ton Report: Advancing Domestic Resources for a Thriving Bioeconomy,” Oak Ridge National Laboratory, Volume 1, 2016.

2:40pm **PB+BI+PS-MoA4 Growth of Plasma-Treated Corn Seeds under Realistic Conditions**, ***Chisung Ahn***, *I.A. Shchelkanov,* University of Illinois at Urbana-Champaign, *J. Gill,* AgReliant Genetics, LLC, *D.N. Ruzic,* University of Illinois at Urbana-Champaign

Plasma treatments of agricultural seeds have been proposed to enhance germination and improve growth rate by elimination of unwanted microbes, water absorption control, introducing functional groups or other effects. In particular, making a plasma-activated medium which has nitrogen as its main component can affect the efficiency of water use in the germination phase. There is also a remarkable complementary effect between plasma treatments and biological pre-treatment. To confirm the plasma effects seen in the lab scale, this work seeks to investigate a variety of seed treatments on an industrial agriculture scale.

In this study, various kinds of plasma were introduced for mass treatment of corn seeds to investigate the germination and growth effect. The seed utilized for the experiment is an elite 111 days yellow dent corn hybrid adapted to the US Midwest. Seven experimental treatments were evaluated: Control, Biological treatment only, Plasma Activated Water (PAW) treatment, Atmospheric Pressure DBD Plasma, Microwave Atmospheric Plasma, Vacuum Plasma and Just Vacuum. The corn seeds were treated uniformly by one-layer arrangement on each stage without burning or blackening by the plasma. Each treatment was performed on a total of 1800 corn seeds. Seed of each experimental condition were treated with the recommended rate of Poncho Votivo with Acceleron, a commercial biological seed treatment that helps protect the seeds from fungus, insects, and nematodes after planting. The 1800 seeds were divided evenly into three replications with 100 seeds planted for each replication at six unique locations across central Illinois. The results of germination, growth, and product yield over the 2017 growing season will be presented.

3:00pm **PB+BI+PS-MoA5 Advanced Control of Plasma Medical Devices**, ***David Graves***, University of California, Berkeley, *A. Mesbah, D. Gidon,* University of California at Berkeley

Atmospheric pressure plasma jets (APPJs) have widespread use in plasma medicine. This presentation aims to demonstrate the importance of using advanced control strategies for safe, reproducible, and therapeutically effective application of APPJs for dose delivery to a target substrate. Key challenges in advanced control of APPJs arise from: (i) the multivariable, nonlinear nature of system dynamics, (ii) the need to constrain the system operation within an operating region that ensures safe plasma treatment, and (iii) the cumulative, non-decreasing nature of dose metrics. To systematically address these challenges, we propose a model predictive control (MPC) strategy for real-time control of a radio-frequency APPJ in argon. To this end, a lumped-parameter, physics-based model is developed for describing the jet dynamics, and cumulative dose metrics are defined for quantifying the thermal and non-thermal energy effects of the plasma on substrate. The closed-loop performance of the MPC strategy is compared to that of basic proportional-integral control. Simulation results indicate that MPC provides a versatile framework for dose delivery in the presence of system disturbances, while fulfilling the safety and practical constraints of APPJ operation. In addition, we demonstrate the use of advanced control in experimental APPJ systems. Advanced control can lead to unprecedented opportunities for effective dose delivery in plasma medicine.

3:20pm **PB+BI+PS-MoA6 Fingerprinting Different Plasma Sources for Biomedical Applications**, ***Katharina Stapelmann***, North Carolina State University, *K. Wende,* INP Greifswald, Germany, *B. Offerhaus,* Ruhr University Bochum, Germany, *C. Verlackt,* University of Antwerp, Belgium, *C. Klinkhammer, F. Kogelheide, M. Havenith,* Ruhr University Bochum, Germany, *A. Bogaerts,* University of Antwerp, Belgium, *P. Awakowicz, J-W. Lackmann,* Ruhr University Bochum, Germany

Cold technical plasmas (CAPs) are under investigation in various fields of industry and medicine. First clinical trials using CAPs for wound healing show promising results. Preliminary results in other fields of plasma medicine, such as cancer treatment, offer promising findings as well. However, the interactions of technical plasmas with biological samples on a molecular level are only partly understood. CAPs generate complex chemical cocktails, having an impact on various biological structures [1]. The impact can vary betweeen different sources, e.g. by employing a DBD in air or a noble gas driven jet. A better understanding of the chemical reactions occuring would allow to tune and adapt plasmas for specific tasks. One prevalent impact of plasma on biological targets has been the chemical modification of thiol groups, which carry out various important tasks in the human body, such as cell signaling and protein structure formation. As thiols are involved in many regulatory and functional processes in tissues, an in-depth understanding of the impact of plasma treatment on thiols is highly relevant for a safe application of plasmas in medicine.

In order to get insight into these interactions, various thiol-containing model substrates, such as the amino acid cysteine and larger target substrates, were investigated with different plasma sources [2,3]. By using a standard target substrate, the impact of various plasma sources can be compared not by means of a physical characterization but by their chemical impact. Stepwise increase of sample complexity allows monitoring how thiols are affected by plasma treatment in an ever more complex environment. The combination of experimental evidence and MD simulations permit a comprehensive overview of chemical processes induced by plasma treatment. This combined approach allows a more throughout investigation of modifications on a molecular level and helps to understand fundamental plasma chemistry processes. Furthermore, knowledge about the substrate chemistry enables the use of test substrates as bio-probes for the investigation of plasma chemistry in other industrial fields [4].

[ 1] Lackmann J-W and Bandow J E 2014 *Appl. Microbiol. Biotechnol.* **98** 6205-13

[ 2] Kogelheide F *et al* 2016 *J. Phys. D: Appl. Phys.***49** 084004

[ 3] Lackmann J-W *et al*. 2015 *J. Phys. D: Appl. Phys*. **48** 494003

[ 4] Offerhaus B *et al*. 2017, accepted in *Plasma Process Polym*.

4:00pm **PB+BI+PS-MoA8 Exploring Plasma Coatings Comprising Vertical Chemical Gradients and Multilayers for Biomedical Applications**, ***Dirk Hegemann***, *M. Vandenbossche, M. Heuberger*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

The common definition of “surface” includes surface atoms and molecules, practically extending at the most some three layers – typically one nanometer. This definition is justified by the fact that many surface properties related to symmetry breaking, such as chemistry, wettability or surface charge are determined by the top most surface layer. The common understanding is that this thin surface region also determines how molecules adsorb onto it. Far less explored are effects due to interactions with deeper subsurface layers, i.e. the region extending over several nanometers underneath the “surface”. This subsurface region, however, might significantly contribute to molecular adsorption via long-range (i.e. few nm) interaction forces; mainly interactions with fixed dipoles, water structuring and Van der Waals interactions. A key factor to make use of these interaction forces thus lies in the hydration of the subsurface region.

Therefore, stable plasma polymer films made of siloxanes were designed that contain a hydrophilic nanoporous base layer terminated by a hydrophobic top coating, nominally 2-12 nm thick. As a model molecule, bovine serum albumin (BSA) was selected and its adsorption was studied on gradient coatings as well as reference coatings immersed in water or phosphate buffered saline (PBS). As a result, protein adsorption was reduced on hydrated hydrophobic/hydrophilic gradient coatings, while dry or dehydrated films show the same adsorption as the reference hydrophobic plasma polymer film.

Furthermore, double layers made of a terminal a-C:H:O plasma polymer layer (1-5 nm thick) on a-C:H:N base layers were investigated comprising a gradient in carboxylic-to-amino groups. Again conditions were selected to obtain stable plasma polymer films when immersed in aqueous environments. Adsorption using the green fluorescent protein (GFP) on different double layers and reference layers were examined. Enhanced protein adsorption was observed for the 1 nm thick terminal layer of a-C:H:O on a-C:H:N as compared to each reference layer.

Hence the vertical nanostructure of a functional surface implies an additional factor to control adsorption processes. Protein adsorption, selectivity and bioactivity can thus be controlled by using subsurface effects being an important finding for biomedical applications such as e.g. tissue engineering.

## Plasma Science and Technology Division
## Room: 23 - Session PS+AS+SS-MoA

## Plasma Surface Interactions
**Moderators:** Michael Gordon, University of California at Santa Barbara, Ying Zhang, Applied Materials, Inc.

1:40pm **PS+AS+SS-MoA1 Exploring the Gas-Surface Interface in NxOy Plasma Surface Modification of Zeolite Materials for Environmental Applications**, ***Angela Hanna****, *E.R. Fisher*, Colorado State University

With increasing concern for environmental health and climate change, there is a greater need to explore fundamental reactivity of pollutant species. Improving the effectiveness of substrates used in vehicular emissions abatement hinges on the ability to discern the contributions of gas-phase species in surface reactions. Here, inductively-coupled $N_xO_y$ plasma systems were investigated to determine relationships between precursor chemistry and gas-surface interface interactions with different substrates. Precursor chemistry was probed via gas-phase diagnostics; time-resolved optical emission data elucidated NO (g) and $N_2$ (g) production kinetics from $N_xO_y$ source gases, whereas steady-state emission and absorbance data provide information on energy partitioning between different degrees of freedom (e.g. vibrational and rotational modes). Specifically, we have determined rotational ($T_R$) and vibrational ($T_V$) temperatures for $N_2$ ($B^3\Pi_g \leftrightarrow C^3\Pi_u$) and NO ($X^2\Pi \leftrightarrow A^2\,\Sigma^+$). $T_R$ and $T_V$ for both molecules show strong positive correlations with applied rf power, as well as a negative correlation with system pressure. $T_V$ is significantly higher than $T_R$ for both $N_2$ and NO, regardless of precursor, with $T_V$ ranging from ~2000 K to >3000K and $T_R$ having values between ~300 K and 1000 K. Ultimately, these data afford significant insight into increased understanding of molecule formation and decomposition pathways, as well as overall plasma chemistry in nitrogen and oxygen-containing plasma systems of interest to pollution abatement. Similarly, interface studies explored the influence of both non-catalytic (e.g. Si wafers) and catalytic (e.g. zeolites, Pt wire) substrates on the gas-phase chemistry in the same plasma systems. X-ray photoelectron spectroscopy and scanning electron microscopy analyses of surface oxidation and morphological changes resulting from plasma processing will be presented. Furthermore, we will describe plasma surface modification of zeolites, in both a static plasma reactor and a rotating drum reactor. Our holistic approach to employing diagnostics tools to characterize the plasma, the surface, and the gas-surface interface suggests a more thorough evaluation of plasma processing for $N_xO_y$ emission control.

2:00pm **PS+AS+SS-MoA2 Effects of Ion induced Damages on Etching Characteristics of ITO Thin Films**, ***Hu Li***, *K. Karahashi*, Osaka University, Japan, *M. Fukasawa, A. Hirata, K. Nagahata, T. Tatsumi*, Sony Semiconductor Solutions Corporation, Japan, *S. Hamaguchi*, Osaka University, Japan

Micro-fabrication of transparent conducing oxides (TCOs), such as tin-doped indium oxide (ITO) and zinc oxide (ZnO), has been performed for optoelectronic devices such as solar panels and head-mounted liquid crystal displays. With the increasing demand of such devices, more efficient and more controllable fabrication technologies for patterning of TCOs are highly required. Reactive ion etching (RIE), which uses energetic reactive ions and typically allows high etch rates and high selectivity over hard masks, may be suitable for high-resolution pattering of TCOs. Hydrocarbon-based non-corrosive gases such as $CH_4$ and methanol have been used for RIE processes of TCOs. However, etching reactions and mechanisms of such processes have not been well understood. Therefore, the goal of this study is to clarify the mechanisms of RIE of TCOs by hydrocarbon-based plasmas.

In this study, sputtering yields of ITO were measured with the use of a mass-selected ion beam system, which allows the injection of only desired ion species with a specified incident energy into a substrate set in an ultra-high vacuum chamber. It has been found that the physical sputtering yield of an ITO film increases with pre-injection of energetic hydrogen (H) or helium (He) ions, which indicates that some atoms of the modified ITO film are less tightly bound and become more amenable to physical sputtering. The X-ray Photoelectron Spectroscopy (XPS) observation of ITO films pre-treated by energetic H or He ion injections has shown that the increase of the sputtering yield cannot be explained by the surface reduction of ITO films. In our preliminary study on ZnO, we have observed by Transmission Electron Microscopy (TEM) that the grain sizes of a ZnO film decrease after the film is exposed to energetic He ion injection. Therefore we surmise that grain sizes of ITO also similarly decrease and consequently the regions of grain boundaries increase after the film is pretreated by energetic H or He ions. By definition, atoms at grain boundaries are less tightly bonded with surrounding atoms than those in the crystalline bulk and therefore the increase of the grain boundaries is likely to contribute to the increase of the sputtering yield of the film.

2:20pm **PS+AS+SS-MoA3 Nitriding Process for Next-generation Semiconductor Devices by VHF (162 MHz) Plasma Source**, ***YouJin Ji***, *K.S. Kim, K.H. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Recently, for low power and high performance of semiconductor devices, the gate oxide thickness is scaled down and gate line-width is reduced. As a result, the role of nitride layer on gate oxide has become crucial to prevent the penetration of boron through thin gate oxide. In addition, high step coverage characteristics that are applicable to fine line patterns in a semiconductor device are also demanded. To keep pace with these detailed requirements, nitriding processes of the deposited silicon oxide employing conventional 13.56 MHz plasma source and $N_2$ as the nitriding gas has been generally utilized. However, 13.56 MHz plasma is difficult to decompose $N_2$ gas sufficiently, therefore, the thickness and nitrogen percentage of the oxynitride layer obtained by nitriding process are limited. In addition, high temperature operation above 200 ºC can also cause the degradation of the device. In this study, a VHF (162 MHz) multi-tile plasma source was used for the decomposition of $N_2$ gas and the effect of the plasma conditions of VHF multi-tile plasma source on the nitridation of silicon oxide at room temperature was investigated. Using the VHF (162 MHz) plasmas, high density nitrogen plasmas with a low electron temperature and high vibration temperature were generated and, with these plasmas, dense oxynitride films with high nitrogen contents could be fabricated. Also, by controlling the plasma conditions, highly uniform oxynitride films with a high step coverage could be also obtained.

2:40pm **PS+AS+SS-MoA4 Defect Generation in Graphene Films by Low-Pressure Inductively Coupled Argon Plasmas Treatments**, *X. Glad, P. Vinchon, S. Boivin, G. Robert-Bigras*, ***Luc Stafford***, Université de Montréal, Canada

For many applications, graphene properties need to be tuned by post-processing techniques, such as plasma treatment. The latter is commonly used as a graphene doping method [1]. However, the decoupling of doping and damage mechanisms may be complex. Typically, damage studies on graphene are carried out using high-energy electron beams [2] or ion beams at energy above a few tens of eV [3]. Nonetheless, a few studies showed that plasma treatment may induce damage on graphite although incident ions transfer less energy to the graphite lattice than the energy threshold displacement ($T_d$ = 15-20 eV) [4]. The literature is strongly lacking systematic and parametric experimental studies of the defects induced in graphene by non-reactive plasma with low-energy ions.

The aim of this study is to investigate the defect formation on graphene films by low-pressure argon inductively coupled plasmas in the very low ion energy range (< 15 eV). To do so, plasma parameters have been assessed by Langmuir probe (LP) and mass spectrometry to determine conditions of fixed ion fluence but different ion energy. Such conditions were obtained by increasing the pressure while lowering the applied rf power and adjusting the treatment time. Raman spectroscopy (RS) was then carried out on each treated graphene sample to evaluate and identify the damage generation.

Our results reveal two contributions on the defect generation: one proportional with the ion energy, the other with the gas pressure. LP and optical absorption measurements have been coupled with a collisional-radiative model to estimate the main energetic species power fluxes (ions, VUV photons, resonant and metastable states). It showed that the ion contribution is the dominant one for each condition. Thus, it seems that with lower ion energy and higher pressure, surface diffusion and redeposition processes become preponderant resulting in a higher density of amorphous carbon found on the graphene sheet, as evidenced by RS. The occurrence of this amorphous matter would explain the high intensity D/G band ratio observed, even at very low-ion energy. Preliminary results thus suggest that, to achieve graphene doping by mild plasma treatment, lower pressure is desirable since minimal production of amorphous carbon is observed.

[1]: A. Dey *et al.*, *Appl. Phys. Rev.* **3** (2016).

[2]: J. Kotakoski, A. V. Krasheninnikov, U. Kaiser, and J. C. Meyer, *Phys. Rev. Lett.* **106** (2011).

[3]: O. Lehtinen, J. Kotakoski, A.V. Krasheninnikov, and J. Keinonen, *Nanotechnology* **22** (2011).

[4]: B. Rousseau, H. Estrade-Szwarckopf, A. L. Thomann, and P. Brault, *Appl. Phys. A: Mater. Sci. Process.* **77** (2003).

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* **Coburn & Winters Student Award Finalist**

### 3:00pm **PS+AS+SS-MoA5 The Role of Plasma Species and Sample Composition on Dense Amorphous Carbon Layer Formation and Polymer Etching Behavior**

***Adam Pranda**, S.A. Gutierrez-Razo, Z. Tomova, J.T. Fourkas, G.S. Oehrlein,* University of Maryland, College Park

Numerous polymer etching models have been previously developed to correlate the structure or composition of the polymer to the plasma etching behavior[1]. A key assumption in these models is that the polymer structure remains homogenous as it is etched. For applications in photoresist pattern transfer, this assumption is not valid since high-energy ion bombardment results in the formation of a heterogeneous structure consisting of a 2-3 nanometer thick dense amorphous carbon (DAC) layer on the polymer surface which mediates the overall etch rate.

In this work, we experimentally examined several key plasma and sample parameters that impact the etching behavior for a set of model polymers and PR193 and PR248-type photoresist. These parameters include plasma composition, fluxes of incident species in the plasma, intensity of ion bombardment-induced surface modifications that affect the etching behavior, polymer chemical composition and molecular structure, along with UV and VUV sensitivity in a plasma environment. From our experimental work, we have found that the thickness and intensity of the DAC layer is highly dependent on the chosen plasma parameters and the polymer composition/molecular structure.

We compare various models of the etching behavior of a polymer based on parameters such as the polymer chemical composition/structure and the flux of incident species in the plasma relative to experimentally observed relationships. Of key significance is the relationship between reactive plasma species and the state of the DAC layer.

One of the experimental correlations we have identified is that a molecular structure consisting of a greater ratio of carbon carbon-type bonding results in a more optically dense DAC layer, which limits the ion flux that reaches the bulk layer, and thus leads to a lower steady-state etch rate. In the presence of any reactive species in the plasma, such as oxygen or fluorocarbon, there is an additional component to the etch rate due to chemical sputtering which results in an increase in the etch yield of the DAC layer. Once the DAC layer is sufficiently depleted, the ion flux reaching the bulk layer increases and thus the bulk etch rate increases as well. Utilizing the experimental results, we seek to arrive at an etching model that can be applied in the development of new photoresists that attain a target steady-state etch rate.

The authors gratefully acknowledge the financial support of this work by the National Science Foundation (NSF CMMI-1449309) and the US Department of Energy Office of Fusion Energy Sciences (DE-SC0001939).

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### 3:20pm **PS+AS+SS-MoA6 Control of Ion Energy Distributions on Insulating Surfaces**

***Tyler List**, T. Ma, V.M. Donnelly, D.J. Economou,* University of Houston

A method for controlling ion energies on insulating substrates using pulsed plasma is presented. A synchronous bias voltage was applied to a boundary electrode in the afterglow of a pulsed plasma, resulting in a positive ion flux to the insulating substrate. To avoid excessive charging of the surface, DC square pulses were periodically applied to the chuck holding the substrate, to attract an electron swarm to the surface and neutralize the surface charge. Surface potential measurements were used to validate the proposed scheme. The effect of pulse width, amplitude, and frequency on the resulting surface potential waveform was examined. A Retarding Field Energy Analyzer was used to measure the ion energy distribution. When corrected for the non-uniform charge distribution prevailing when the applied RF frequency is less than the ion sheath transit frequency, the IED was similar to that predicted by a mathematical model of the system. Etching of quartz discs and 1000 nm-thick $SiO_2$ films, thermally grown on Si wafers, was also performed. For both types of substrates, beyond an etching threshold, the etching rate increased linearly with the square root of chuck bias. No clear effect of the boundary electrode bias voltage on the etching rate was observed. The behavior of etching rate as a function of the (DC chuck bias) pulse width mirrored the dependence of surface potential on pulse width. Work supported by NSF and DOE.

### 4:00pm **PS+AS+SS-MoA8 Ultra-high $Si_3N_4$ to $SiO_2$ Selective Etching by Fluorocarbon Based Remote Plasma**

***Chen Li**,* University of Maryland, College Park, *T. Hofmann, K. Edinger,* Carl Zeiss SMT GmbH, *G.S. Oehrlein*, University of Maryland, College Park

Plasma etching processes capable of highly selective $Si_3N_4$ to $SiO_2$ removal are increasingly required in fabrication of current integrated circuit devices. We report fluorocarbon (FC) based remote plasma etching processes for $Si_3N_4$ and $SiO_2$ substrates using inductively coupled plasma (ICP) and electron cyclotron wave resonance (ECWR) plasma reactors. For the remote plasma operating conditions direct ion bombardment of the sample surface is prevented and etching is primarily due to chemical reactions by neutral radicals. Such conditions can be realized by either high processing pressure for a remote ICP source or a neutralization plate for an ECWR source. Combinations of fluorocarbon gases, e.g. $CF_4$, with $O_2$ and $N_2$ additives have been evaluated. Etching behavior and surface properties are monitored using *in situ* ellipsometry. Optical emission spectroscopy (OES) has been used to evaluate the plasma gas phase chemistry. We show that ultra-high $Si_3N_4$ to $SiO_2$ etching selectivity can be achieved under remote plasma conditions in both reactors, and that control of the feed gas chemistry plays a key role. As is well-known, low levels of $O_2$ increase oxidation of FC gases and atomic F generation, which leads to increasing $Si_3N_4$ etch rate, whereas for high $O_2$ levels the F concentration is reduced and surface oxidation takes place. For these F-rich remote plasma conditions, $SiO_2$ is hardly etched and $Si_3N_4$ to $SiO_2$ etching selectivity of 7 and 87 were observed for the ICP and ECWR system, respectively. The observed etching behavior will be discussed using surface chemical studies of $Si_3N_4$ and $SiO_2$ by vacuum transferred x-ray photoelectron spectroscopy (XPS).

### 4:20pm **PS+AS+SS-MoA9 Effect of Temporal Variation of Discharge on Photon-induced Interface Defects in Pulse-modulated Inductively Coupled Plasma**

***Yasufumi Miyoshi**, M. Fukasawa, K. Nagahata*, Sony Semiconductor Solutions Corporation, Japan*, K. Ishikawa, M. Sekine, M. Hori,* Nagoya University, Japan*, T. Tatsumi*, Sony Semiconductor Solutions Corporation, Japan

It is important to reduce photon-induced interface defects, which degrade the performance of electric devices. Ishikawa et al. reported that using pulse-time-modulated plasma reduces UV photon-induced defects [1]. In this study, we investigated how temporal variation of the discharge affected these defects in pulse-modulated $Ar/CF_4/O_2$ inductively coupled plasma (ICP).

In this study, we varied the ICP source pulse frequency (0.5–20 kHz) and duty ratio (50–100%) as well as the gas ratio of $Ar/CF_4$. To investigate the UV radiation damage, the interface-trap density ($D_{it}$) was measured by using on-wafer pallet for plasma evaluation (PAPE) [2]. We used $D_{it}$, which is proportional to the UV fluence from discharge, as an indicator of UV damage. Temporal changes in the optical emission spectroscopy (OES) intensity of pulsed plasma were also investigated.

The measured $D_{it}$ was lower than that in the CW at lower frequencies but was higher at higher frequencies (> 10 KHz). Increasing the frequency increased $D_{it}$, which reached a maximum at 10 kHz for $Ar/CF_4 = 1$, and then decreased $D_{it}$. Using a lower $CF_4$ ratio shifted the maximum $D_{it}$ to a lower frequency.

This frequency-dependent behavior comes from the transient behavior of the pulsed ICP. Time-resolved OES revealed an optical emission overshoot after ignition caused by the variation in the electron temperature and number density in the early ON phase. The number of overshoots increased with increasing frequency, increasing the UV fluence and $D_{it}$. At higher frequencies, the variation in the electron temperature and number density were suppressed due to stepwise ionization from residual long-lived metastable species in the early ON phase [3]. This behavior considerably decreased overshoot amplitude, in turn decreasing the UV fluence and $D_{it}$. At the lower $CF_4$ ratio, quenching of the metastable species by $CF_4$ decreased and the lifetime of the metastable species during the OFF phase likely increased. Therefore, we presume that, at the lower $CF_4$ ratio, the overshoot amplitude began to decrease at a lower frequency than when $Ar/CF_4 = 1$ and the maximum $D_{it}$ consequently shifted to a lower frequency.

These results show that controlling the temporal variation of a pulse-modulated plasma is essential to reduce the photon-induced damage it causes during plasma processes.

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[2] M. Fukasawa et al., Jpn. J. Appl. Phys. **52** (2013) 05ED01.

[3] S. K. Monfared et al., J. Phys. D: Appl. Phys. **46** (2013) 425201

### 4:40pm **PS+AS+SS-MoA10 Surface Mechanisms on Dielectric Surfaces Exposed to Low Pressure Glow Discharge and Atmospheric Pressure Plasma Jets**

***Olivier Guaitella**, A.S. Morillo-Candas,* Ecole Polytechnique - CNRS, France*, A. Sobota*, Eindhoven University of Technology, The Netherlands*, E. Slikboer, D. Marinov,* Ecole Polytechnique - CNRS, France, *B. Klarenaar, R. Engeln*, Eindhoven University of Technology, The Netherlands, *V. Guerra*, Instituto Superior Tecnico, Lisbon, Portugal **INVITED**

New applications of Non Thermal Plasmas (NTP) at atmospheric pressure such as biomedical applications, air treatment or CO2 recycling are growing rapidly with the better control of these plasma sources. All these applications rely on the effect of a transient plasma discharge with complex surfaces such as porous catalyst or biological tissues for instance. The interaction of plasma with surfaces is always a very challenging topic because of the multiplicity of phenomena modifying the surface but also because of the reverse influence of the substrate on the plasma properties. Therefore most of the studies dedicated to plasma surface interactions are performed with very low pressure plasmas and ideal model surfaces. No conclusion can be drawn on surface mechanisms if the plasma in contact with the surface is not well characterized while being in contact with the surface of interest.

The originality of the approach we have developed consists in the utilization a low pressure (1-10 mbar) pulsed dc discharge for investigation of elementary processes on the surface of real catalytic materials that are also studied in atmospheric pressure DBDs.

The pulsed glow discharge allow us to measure the dynamic of plasma parameters (Electric field, Gas temperature, radical densities, vibrational excitation etc…) to give constraints to kinetics models allowing us to distinguish between gas phase reactions and the role of elementary surface processes such as O atoms recombination or molecule conversion on surface. Various diagnostics have been used in the gas phase including Doppler broadened TALIF (for O atoms density and gas temperature), or step scan FTIR (for vibrational temperature of $CO_2$ and CO). Infrared absorption is performed in transmission directly through catalyst pellets exposed to the same plasma to investigate adsorbed molecules.

In parallel, other diagnostics are being developed to obtain electric field, temperature profile and adsorbed species on surfaces exposed to atmospheric pressure plasma sources. A kHz plasma jet configuration is used for its reproducibility as a first model plasma source for studying ionization wave interaction with surfaces. Surface electric field, charge deposited and is obtained under controlled atmosphere from polarization technique based on Pockels effect. Infrared absorption in transmission through catalyst samples is also used under plasma jet exposure.

The use of reproducible plasma sources allowing the combination of gas phase diagnostics and in situ surface diagnostics gives a new perspective on the importance of surface processes even at elevated pressures.

## Scanning Probe Microscopy Focus Topic
## Room: 10 - Session SP+2D+AS+NS+SS-MoA

### Probing Electronic and Transport Properties

**Moderators:** Phillip First, Georgia Institute of Technology, Chuanxu Ma, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

1:40pm **SP+2D+AS+NS+SS-MoA1 Probing Atomic and Electronic Structures of 2D Electronic Materials and their Heterostructures**, ***Chih-Kang Shih***, University of Texas at Dallas **INVITED**

The emerging atomic layer materials offer a remarkably wide range of building blocks of nanostructures ranging from metals (e.g. graphene), large gap insulators (BN), to semiconductors (transition metal dichalcogenides and black phosphorous). Key advantages of these van der Waals materials include a broad span of energy gaps, flexibility of stacking different types of materials to form heterostructures, tunability in material properties by doping and strain, and the relative ease of integration with other electronic and photonic devices. This talk will be focused on the usage of scanning tunneling microscopy and spectroscopy to probe the atomic and electronic structure of transition metal dichalcogenides (TMDs) and their heterostructures, including both vertical and lateral structures.

I will first introduce a comprehensive form of scanning tunneling spectroscopy (STS) which allows us to probe not only the quasi-particle band gaps but also the critical point energy locations and their origins in the Brillouin Zone (BZ) can be revealed using this comprehensive form of STS. By using this new method, we reveal the systematic trend of the critical point energies for TMDs due to atomic orbital couplings, spin-orbital coupling and the interlayer coupling. By using the vertically stacked MoS2/WSe2, I will show how interlayer coupling can be used as a new designing parameter to create a lateral 2D electronic superlattices. I will then turn attention to MoS2/WSe2 lateral heterostructure where I will show a novel method to probe 2D strain tensor and how the strain changes the band profile as well as the band alignment at the interface.

2:20pm **SP+2D+AS+NS+SS-MoA3 SP-STM Study of Antiferromagnetic CuMnAs Thin Film**, ***Giang Nguyen***, Oak Ridge National Laboratory, *P. Wadley, R. Campion, K. Edmonds,* University of Nottingham, UK, *F. Maccherozzi, S. Dhesi,* 3Diamond Light Source, UK, *T. Jungwirth*, University of Nottingham, UK, *A.-P. Li*, Oak Ridge National Laboratory

Antiferromagnetic (AFM) tetragonal CuMnAs thin films have attracted great research interest recently, largely due to the capability of manipulating and detecting of their AFM states with ordinary electric current. Here we report a study on a CuMnAs thin film, grown epitaxially on GaP(001) substrates, using Spin-Polarized Scanning Tunneling Microscopy (SP-STM). An arsenic capping layer is used to protect the sample during transferring through the air which is able to be subsequently removed from the surface by thermal annealing. Atomic resolution STM topographic images of CuMnAs surface are achieved which shows an interesting surface reconstruction. Scanning tunneling spectroscopy (STS) is performed to explore the electronic structure of the thin film as well at the surface step edge. SP-STM study in combination with X-ray magnetic linear dichroism-photoelectron emission microscopic (XMLD-PEEM) measurements provides further understanding of the antiferromagnetic domain structure.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

2:40pm **SP+2D+AS+NS+SS-MoA4 Probing Spin-Dependent Chemical Potential in Topological Insulator by Spin-Polarized Four-Probe Scanning Tunneling Microscopy**, ***Wonhee Ko***, *S.M. Hus,* Oak Ridge National Laboratory, *Y.P. Chen,* Purdue University, *A.-P. Li,* Oak Ridge National Laboratory

Conversion between the charge and the spin signal is a core technology for detection of many spin-related phenomena and for the realization of spintronic devices. Topological insulators are promising candidate for such purpose because of their surface states with non-trivial spin texture. The surface states electrons have the spin and the momentum locked to each other, so the electrical current can induce the uneven shift in the spin-dependent chemical potential for different spin directions. In this talk, we utilized spin-polarized four-probe scanning tunneling microscopy to probe the spin-dependent chemical potential of the topological insulators. Utilizing ferromagnetic tips and variable probe-spacing measurements, we detected non-vanishing spin-dependent chemical potential induced by the charge current. Various tip and surface conditions were tested to confirm its origin from the spin of charge carriers through the surface states. The result demonstrates the generation of excessive spins only by electrical means in topological insulators, which would become the critical component for the future spintronic applications.

This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

3:00pm **SP+2D+AS+NS+SS-MoA5 Spin-charge Transport Phenomena on the Atomic Scale Studied by Multi-probe STM**, ***Christoph Tegenkamp***, Leibniz Universität Hannover, Germany **INVITED**

Low dimensional metallic structures, e.g. quantum wires and films on surfaces, reveal fascinating phenomena of condensed matter physics. Among others, 2D-superconductvity, formation of charge density waves and topologically protected edge states were realized lately with atomic precision and directly probed by electronic transport. Generally, the surface science approach benefits from the fact that the low dimensional systems can be comprehensively characterized and manipulated in view of their atomic structure and electronic bands. This is a prerequisite to understand electronic transport on the atomic scale.

In this talk I will introduce the technique of surface sensitive transport by means of 4-tip STM technique and highlight some recent examples of our group from seemingly different fields, e.g. spintronic, correlated materials and mesoscopic physics. The talk covers spin-orbit coupling related phase transitions in quasi 1D atomic wire structures (Au/Si(553), Pb/Si(557) [1,2]) as well as ballistic transmittance of electrons in epitaxially grown graphene nanostructures on SiC(0001) [3-5].

[1] C. Tegenkamp, et.al. PRL 109, 266401 (2012)

[2] C. Brand, et.al. , Nat. Comm. 6, 8118 (2015)

[3] J. Baringhaus ,et.al., Nature 506, 349 (2014)

[4] J. Baringhaus et.al. Sci. Rep. (Nature) 5, 9955 (2015)

[5] J. Baringhaus et.al. PRL. 116, 3186602 (2016)

4:00pm **SP+2D+AS+NS+SS-MoA8 Site-specific Superconducting Atomic Contacts Studied by Scanning Tunneling Microscopy**, ***Yukio Hasegawa***, The Institute for Solid State Physics, The University of Tokyo, Japan **INVITED**

In the trend of miniaturization of devices, electrical conductance through atomic-scale contacts is of significant importance for practical application of atom switch and single molecular devices. Because of unknown atomic geometry at the junction, however, the measured conductance often fluctuates. Here in this study we have studied the conductance properties of atomic superconducting point contact with precise control of contact geometry to investigate atomic details of conductance channel formation through it.

Using a low-temperature scanning tunneling microscopy (STM), we measured the conductance between the tip and sample surface from the tunneling to contact regimes [1]. By precisely positioning the tip on atomically specific sites of a sample surface such as on-top and hollow sites, site-specific conductance evolutions were obtained. We found using a Pb tip and Pb thin film as contact forming materials the conductance at point contact is larger at hollow site than at on-top site. Furthermore, it is found that the relation of the conductance measured is reversed just before the contact formation; at 20 pm away from the contact the conductance of the hollow site is smaller than the on-top site. These peculiar conductance behaviors can be explained by the attractive chemical force and subsequent conductance channel formation between the tip apex atom and surface atoms of the thin film.

Since the measurements were performed at low temperature (1.6 K) below the superconducting critical temperature of both materials, we obtained the evolution of the Josephson current and subharmonic in-gap structures due to multiple Andreev reflection (MAR) in the conductance spectra. From the analysis of the MAR structures, the complete set of transmission probability of conduction channels, which is often called personal identification number (PIN) of the junction as it determines all the coherent transport properties, was successfully extracted [2]. We found again site dependent evolution of transmission probabilities and the number of active conduction channels at the contact formation. We will discuss on the mechanism of channel formations based on comparison with the results of theoretical analysis.

References

[1] H. Kim and Y. Hasegawa, Phys Rev Lett 114, 206801 (2015)

[2] H. Kim, M. Kawamura, T. Kato, T. Ozaki, and Y. Hasegawa, in preparation.

4:40pm **SP+2D+AS+NS+SS-MoA10 The Difference between Electron and Hole Dopant of Magnetic Element to the Superconductivity in BaFe$_2$As$_2$**, ***Qiang Zou***, *L. Li, A. Sefat, D.S. Parker, Z. Gai*, Oak Ridge National Laboratory

The effect of magnetism and spin excitation in the Fe-based superconductors (FeSC) is crucial to understand their superconductivity. Both electron-(Ni) and hole-(Cr) dopant of magnetic elements could lead to suppression of the magnetic/structural phase transition in BaFe$_2$As$_2$. However, the Cr doped BaFe$_2$As$_2$ doesn't show the superconductivity. Using scanning tunneling microscopy/spectroscopy, here, we compared the electronic properties of BaFe$_2$-xNixAs$_2$ and BaFe$_2$-xCrxAs$_2$ at various temperatures. Our results will shed the light on the microscopic understanding of relation between the superconductivity and magnetism in the FeSC. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

5:00pm **SP+2D+AS+NS+SS-MoA11 Rapid Measurement of I-V Curves in Scanning Probe Microscopy via Bayesian Inference**, *S. Somnath, K. Law, R. Archibald, S.V. Kalinin, S. Jesse,* ***Rama Vasudevan***, Oak Ridge National Laboratory

Current-voltage (IV) curve acquisition is the oldest and most common spectroscopic method implemented on virtually every scanning probe microscope (SPM) available. Though in use for three decades, the basic measurement has not altered substantially in this time-frame, with the current being detected during DC pulses applied to the SPM tip. Such measurements include both a delay time after each DC voltage change (to reduce parasitic capacitance influence), as well as a an integration time, to reduce noise, limiting typical measurements to a few Hz at most. Here, we introduce a new method for IV curve acquisition, based on an AC-excitation of the SPM tip, in combination with full information acquisition from the current amplifier and Bayesian inference. IV curves are acquired on a model ferroelectric system, at rates ~500x faster than the current state of the art, with higher spatial and spectral resolution. The obtained results offer a complementary channel of information to supplement existing piezoresponse force microscopy studies, allowing to probe disorder at the nanoscale. Bayesian inference further allows quantification of the capacitance contribution, which can be utilized to estimate the dielectric constant of the ferroelectric, with results agreeing with reported values. These studies highlight the utility of both complete information acquisition, and Bayesian inference, in dramatically increasing the acquisition rates of data from SPM.

This research was sponsored by the Division of Materials Sciences and Engineering, BES, DOE (RKV, SVK, SS). This research was conducted and partially supported (SJ) at the Center for Nanophase Materials Sciences, which is a US DOE Office of Science User Facility. Bayesian inference portion was sponsored by the Applied Mathematics Division of ASCR, DOE; in particular under the ACUMEN project (KJHL, RA).

## Surface Science Division
## Room: 25 - Session SS+AS+HC-MoA

## Surface Science for Energy and the Environment

**Moderators:** Steven Bernasek, Yale-National University of Singapore, Bruce Koel, Princeton University

2:20pm **SS+AS+HC-MoA3 Photochemistry of CO, Acetone and O$_2$ on Reduced Rutile TiO$_2$(110)**, ***Greg Kimmel***, *N.G. Petrik, M.A. Henderson*, Pacific Northwest National Laboratory **INVITED**

TiO$_2$ is an important photocatalyst with many practical applications. However, a fundamental understanding of the thermal and non-thermal reactions on TiO$_2$ surfaces is still lacking. We use ultrahigh vacuum (UHV) surface science techniques to investigate in detail representative reactions on single crystal rutile TiO$_2$(110). For this talk, I will focus on the ultraviolet (UV) photon-stimulated reactions of CO, acetone and oxygen adsorbed on TiO$_2$(110). For CO co-adsorbed with O$_2$, CO$_2$ is produced during UV irradiation. The CO$_2$ preferentially desorbs in the plane perpendicular to the bridge-bonded oxygen (BBO) rows at an angle of 45°. Furthermore, the production rate of CO$_2$ is zero when the UV irradiation starts and reaches a maximum value at intermediate times before decaying at longer times. The results demonstrate that the photooxidation of CO is a multi-step reaction that proceeds through a metastable intermediate state that is oriented perpendicular to the BBO rows. This state is consistent with an O-O-C-O state found via density functional theory. For acetone co-adsorbed with oxygen, previous research suggests that a thermal reaction between acetone and adsorbed oxygen to form an acetone diolate precedes the photochemistry. During UV irradiation, a methyl radical is ejected leaving acetate on the surface. Using infrared reflection absorption spectroscopy (IRAS), we have identified the acetone diolate. We have also measured the angular distribution of the photodesorbing methyl radicals. Consistent with its ejection from acetone diolate, we observe a peak in the distribution at ~45° in the plane perpendicular to the BBO rows. However, a second photodesorption peak normal to the surface indicates that a second, previously unidentified, reaction channel is available. We attribute this second channel to the photo-induced formation of an enolate intermediate. When only O$_2$ is adsorbed on TiO$_2$(110), its photochemistry depends on the coverage. For small coverages, only ~14% desorbs while the rest either dissociates during UV irradiation, or remains molecularly adsorbed on the surface. For the maximum coverage of chemisorbed oxygen, the fraction of O$_2$ that photodesorbs is ~45%. While photo-generated holes are responsible for the O$_2$ photodesorption, photo-generated electrons are responsible for the photo-induced O$_2$ dissociation. In general, these studies provide new insights into mechanisms responsible for the photochemistry of small molecules on TiO$_2$.

3:00pm **SS+AS+HC-MoA5 The Role of Band Alignment in Ketone Photooxidation on TiO$_2$(110)**, ***Amanda Muraca***, Stony Brook University, *M.G. White*, Brookhaven National Lab and Stony Brook University

Organic photooxidation processes on the TiO$_2$(110) surface often show enhanced photoproduct yields in the presence of oxygen. For a series of simple ketones, it has widely been established that the photoactive surface species is a ketone-oxygen complex ($\eta_2$-ketone diolate) formed by interaction with O-adatoms, whereas the $\eta_1$-bound ketone is mostly photo-inactive.[1] The question remains, however, why the ketone-oxygen complexes are more photoactive than the adsorbed ketone alone. One possible explanation is that the diolate species have higher densities of molecular states near the valence band maximum (VBM) of TiO$_{2,}$ where resonant electron transfer to thermalized holes is expected to occur. To test this hypothesis, a series of methyl photoyield measurements, with and without co-adsorbed oxygen, were compared for a number of substituted ketone molecules (R(CH$_3$)CO; R = H, methyl, ethyl, butyl, propyl, phenyl, and trifluoromethyl) with varying ionization potentials (IPs). Experimentally, we observe a near linear correlation between the methyl photoproduct enhancement yields (diolate vs ketone) and the IPs of the bare ketone. These results suggest that as the ketone IP moves to higher energies, its hybridized orbitals move further (deeper) from the VBM and thereby exhibit a larger photoproduct enhancement when forming the ketone-diolate. This explanation points to orbital band alignment as the key factor determining ketone photoxidation activity, but this conclusion is largely based on the gas-phase properties and well established ideas of substituent effects. To gain more insight on our experimental results, we are currently using electronic structure calculations, both cluster models and periodic DFT, that could potentially provide more detail on band alignments for these molecules bound on the TiO$_2$(110) surface.

1. M. A. Henderson, N. A. Deskins, R. T. Zehr, M. Dupuis, *J. Catal.***2011**, *279*, 205; N. G. Petrik, M. A. Henderson, G. A. Kimmel, *J. Phys. Chem. C* **2015**, *119*, 12262.

3:20pm **SS+AS+HC-MoA6 Storing Gases in Nanoporous Metal organic Frameworks Materials with a Surface Barrier Layer**, ***Kui Tan***, the University of Texas at Dallas, *S. Jensen, S. Zuluaga,* Wake Forest University, *E. Fuentes, E. Mattson, J.-F. Veyan,* University of Texas at Dallas, *H. Wang, J. Li,* Rutgers University, *T. Thonhauser,* Wake Forest University, *Y.J. Chabal*, University of Texas at Dallas

Enhancing gas adsorption in porous materials such as metal organic frameworks (MOFs) is critical to many technologies such as energy storage and gas capture and separation**.** In contrast to the previous efforts focusing on chemically modifying the entire MOFs structure to increase the affinity to gas molecules, in our recent work [Nature Communications, 2016, 7, 13871], we demonstrated an entirely new approach to trap small molecules by depositing a layer of ethylenediamine (EDA) on the external surface without penetrating inside the bulk of crystals in the gas loading process, and forms a monolayer cap that can effectively trap weakly adsorbed molecules (CO, $CO_2$, $SO_2$, $C_2H_4$, NO) or prevent their penetration. A combination of surface sensitive techniques *in-situ* infrared spectroscopy, X-ray photoelectron spectroscopy with gas cluster sputtering, low energy ion spectroscopy, and *ab initio* calculations demonstrate that the EDA layer is less than 1nm thick and arranges in a manner that increases CO diffusion barrier by ~24 times. Motivated by this finding, we further explore other capping media to store molecules inside MOFs. The latest experimental results suggest at least two ways: one is the deposition of a thin layer of aluminum oxide exclusively onto the external surface of certain MOFs with a narrower pore size (< 1.2 nm) by using common atomic layer disposition (ALD) precursor trimethylaluminum (TMA). Aluminum oxide is not able to grow inside MOFs since the reactivity of TMA with adsorbed $H_2O$ is significantly reduced due to nano-confinement effects; another convenient way is post-exposure of gas-loaded MOF-74 to $NH_3$. $NH_3$ is preferentially adsorbed on the outer layer of MOFs crystals during the controlled exposure time (<10 min), as a result of which, the diffusion barrier of small gas molecules such as CO, $CO_2$, $SO_2$ in $NH_3$ decorated MOFs channels dramatically increases by the hydrogen bonding interaction. The ability to create surface barrier layers on MOFs external surfaces constitutes a new paradigm for trapping small gas molecules within nanoporous materials in general, and in MOFs in particular.

4:00pm **SS+AS+HC-MoA8 Active Species and Structures of Modified Oxide Catalysts for the Oxygen Evolution Reaction (OER)**, *Z. Chen,* Princeton University, *L. Cai,* Xi'an Jiaotong University, China, ***Bruce Koel***, Princeton University

Transition metal oxides (TMOs) are promising catalysts for oxygen evolution with the potential to replace precious metal-based catalysts (e.g. $IrO_x$ and $RuO_x$). Significant improvements to the OER activity of TMOs have been made by tailoring the morphology and crystal structure of the catalysts, incorporating dopants, as well as using conductive supports. However, clear structure-activity correlations remain elusive because of the complex composition and structure of TMO catalysts. In this contribution, we utilizing a range of spectroscopic techniques for characterization of Ce-modified copper oxide ($CuO_x$) and Ni-modified cobalt (oxy)hydroxides to reveal the OER active species and structures of these catalysts. In the case of Ce-modified $CuO_x$, Ce incorporation (6.9 at%) into $CuO_x$ led to 3.3 times greater OER activity compared to pure $CuO_x$ and this is coincident with significant structural changes due to an increasing amount of disorder. By combining X-ray photoelectron and Raman spectroscopy techniques, a strong correlation between OER performance with tetravalent Ce ($Ce^{4+}$) ions was observed up to a concentration corresponding to $CeO_2$ phase segregation. We propose a strong promoting effect of $Ce^{4+}$ for OER in this system. In the case of Ni-modified $CoO_xH_y$, operando Raman spectroscopy was used to reveal a drastic transformation of a spinel $Co_3O_4$-like structure into a more active (oxy)hydroxide structure under applied potential. Such a transformation was only observed in the presence of uniformly distributed Ni ions. These two examples, i.e. the promoting effect of $Ce^{4+}$ and the formation of active OER structures in Ni-modified $CoO_xH_y$, reveal the importance of chemical state and local structure considerations for the rational design of OER oxide-based OER catalysts.

4:40pm **SS+AS+HC-MoA10 Cactus Based-Mucilage as an Alternative Natural Dispersant for Oil Spill Applications**, ***Fei Guo***, *D. Steebins, S. Thomas, R. Toomey, N. Alcantar,* University of South Florida

Functional surfactants from natural materials have the advantage of being biodegradable and can be obtained through sustainable agriculture. The functional natural surfactants was extracted from the *Opuntia ficus indica* cactus plant. The properties of the cactus plant-based mucilage were studied on the surface tension change, droplet size, and stability of Oil in Water (O/W) emulsions, toxicity, and dispersion effectiveness. Surface tension test was used to quantify the variation of surface tension of the Oil/Water (O/W) emulsion with the application of cactus mucilage and conventional dispersants (COREXIT 9500). The factors and the levels of each factor were as follows: DOR (mg/mg) (control, 1:200, 1:100, 1:50, and 1:20), Volume ratio of oil (3 and 6% v/v). It is observed that the application of NE reduced the surface tensions of the O/W emulsions. It also can be seen that the surface tensions of the O/W emulsion displayed a distinction among the different DORs at a lower volume ratio of oil. The results of the dispersion obtained using mucilage extracts were compared with using COREXIT 9500. The surface tensions of emulsions with cactus mucilage were similar as that with COREXIT 9500. The average droplet size in the systems with cactus mucilage were smaller when compared with the systems using the COREXIT 9500. Smaller droplet size implies higher emulsion stability, and may improve the biodegradation of oil. The baffled flask test was conducted to determine the influence of three environmental factors with cactus mucilage on oil dispersion. The percentage effectiveness of the dispersion was the response variable for this experiment. The factors and the levels of each factor were as follows: DOR (mg/mg) (control, 1:200, 1:100, 1:75, 1:50, 1:35, and 1:20), salinity of the synthetic seawater (10 and 35 PSU), and mixing speed (150, 200, and 250 rpm). The results showed that the dispersion effectiveness increased as DOR increased. There was also a good distinction among the different DORs. The increasing of the amount of cactus mucilage caused a reduction of the interfacial tension of O/W emulsion which made it easier to form the oil droplets. The cactus mucilage performed better at a lower salinity. The toxicity of the mucilage and COREXIT 9500 were evaluated by a standard EPA toxicity test using Daphnia magna colonies exposed to NE mucilage extract in concentrations ranging from 0 to 2000 mg/L for 48 hours. It has shown that mucilage can be classified as practically non-toxic to the Daphnia magna colonies with a $LC_{50}$ above 500 mg/L, while the $LC_{50}$ of COREXIT 9500 was below 2 mg/L, which is moderately toxic to the Daphnia magna colonies.

5:00pm **SS+AS+HC-MoA11 The Effect of Humidity on Chemical Interactions at Hybrid Interfaces: An In Situ Investigation of Polymer/Metal Oxide Bonds**, ***Sven Pletincx***, Vrije Universiteit Brussel, Belgium, *L. Trotochaud,* Lawrence Berkeley National Laboratory, *L.-L. Fockaert*, TU Delft, Netherlands*, A.R. Head, O. Karslıoğlu,* Lawrence Berkeley National Laboratory*, J.M.C. Mol,* TU Delft, Netherlands*, H. Bluhm,* Lawrence Berkeley National Laboratory*, H. Terryn, T. Hauffman*, Vrije Universiteit Brussel, Belgium

Probing interactions at the interface of polymer coatings and passivated metal oxide surfaces under humid conditions has the potential to reveal the local chemical environment at solid/solid interfaces under real-world, technologically relevant conditions. Common surface sensitive analysis techniques only operate under vacuum conditions, making it impossible to probe environmental effects *in situ*. Stability of formed bonds in aqueous environments between carboxylic acid functional groups of a polymer and a hydroxide surface of aluminum oxide has a great relevance to a broad range of applications. Although this region is very important for understanding adhesion of the polymer coating, it is very challenging to get useful information directly from the solid/solid interface, let alone characterize the effect of water on the formed chemical bonds.

Recent developments in the field of ambient-pressure photoelectron spectroscopy (APXPS) make it possible to set up a novel approach with respect to interface studies. [1] This is done by making the polymer layer sufficiently thin to access the interface with this surface analysis technique. A broad range of relative humidity can be simulated in the analysis chamber, to unravel interfacial chemistry changes of the hybrid system *in situ.* Here, we show that APXPS with a conventional X-ray source can be used to study the effects of water exposure on the interaction of acrylic coatings with aluminum oxide. [2]

Complementary *in situ* ATR-FTIR Kretschmann experiments on a similar model system are conducted. An Al layer is sputtered on an IR transparent crystal, the IR signal at the interface is amplified because of the Kretschmann effect and a near-interface spectrum of the oxide/polymer surface is obtained. This way, we have direct access to the interface, and the influence of an above-the-polymer electrolyte (i.e. $H_2O$) can be probed. An integrated setup of ATR-FTIR Kretschmann and Odd Random Phase multisine Electrochemical Impedance Spectroscopy (ORP-EIS) allows to probe the transport of water (and other ions) through the polymer towards the interface. The subsequent interface processes can be followed with infrared spectroscopy while simultaneously the protective properties of the overall hybrid system are studied by ORP-EIS. [3]

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## Thin Films Division
## Room: 20 - Session TF-MoA

## Emerging Applications for ALD

**Moderators:** Mark Losego, Georgia Institute of Technology, Virginia Wheeler, U.S. Naval Research Laboratory

1:40pm **TF-MoA1 Probe the Reaction Chemistry during Atomic Layer Deposition onto $CH_3NH_3PbI_3$**, ***Qing Peng***, *X.Z. Yu*, University of Alabama

The rapid development of organic-inorganic hybrid halide perovskites, represented by $CH_3NH_3PbI_3$, based solar cells is one of the major scientific breakthroughs of recent years. It is superior optoelectronic properties inspired applications beyond solar cells, including LEDs, transistors, and sensors. Thin metal oxide coatings are promising electron extraction layer, moisture barrier, electron injection layer, electron blocking layer, and high-k dielectrics for semiconducting $CH_3NH_3PbI_3$. Atomic layer deposition (ALD) is a promising method to directly put these metal oxides onto $CH_3NH_3PbI_3$. The pure heterogeneous reaction mechanisms provide ALD the capability to deliver conformal films on substrates of complex morphology with sub-nanometer control of the composition and thickness of the film. On the other hand, the heterogeneous-reaction-driven film growth mode in ALD process demands a molecular level understanding of the heterogeneous reaction chemistry. In this presentation, we will show the surface reaction mechanisms of ALD oxide on $CH_3NH_3PbI_3$ by using a suite of in-situ and ex-situ analytic methods. Our results show that the heterogeneous reaction chemistries of ALD during the nucleation stage of ALD oxide on $CH_3NH_3PbX_3$ is complex. Based on these fundamental understandings, we will further show that one can control the formation of the oxide layer by ALD through the careful control of the ALD chemistry and process conditions.

2:00pm **TF-MoA2 Digital Doping of ALD Nb:$VO_2$ Thin Films for Thermochromic Applications**, ***Alexander Kozen***, *M. Currie, B.P. Downey, C.R. Eddy, Jr., V.D. Wheeler*, U.S. Naval Research Laboratory

Vanadium Dioxide ($VO_2$) is a thermochromic material that undergoes a first order crystalline phase transition at a critical temperature ($T_c$) of 68˚C. This structural phase transition is accompanied by major changes in electrical and optical properties, particularly in the infrared. As such, $VO_2$ is suitable for many applications including microbolometers, adaptive thermal coatings, and passive spacecraft thermal shielding.

While the $T_c$ of $VO_2$ is appropriate for many current applications, it is desirable to modify the $T_c$ to other values for improved performance of current applications or to address new emerging application needs. The $T_c$ of $VO_2$ has been shifted by doping with other transition metals on the order of 1-5%.[1], [2], however these doped $VO_2$ films were deposited by PLD, MBE, and sputtering, all line of sight physical vapor deposition techniques.

We demonstrate digital doping of ALD Nb:$VO_2$ by incorporation of ALD $Nb_2O_5$ (TBTDEN + $O_3$) into the conventional ALD $VO_2$ process (TEMAV + $O_3$). Inclusion of Nb into the ALD $VO_2$ process in amounts between 1% and 5% makes minimal impact on as-deposited film morphology. After annealing, the Nb:$VO_2$ films also exhibit minimal physical changes from their undoped analogues. We find that Nb doping can lower the $T_c$ of the $VO_2$ films by -13.5˚C/Nb% while maintaining acceptable optical modulation behavior, critical for use of doped $VO_2$ in emerging applications.

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2:20pm **TF-MoA3 Mechanisms in Organic and Hybrid Organic-Inorganic Molecular Layer Deposition**, ***David Bergsman****, *S.F. Bent*, Stanford University

Molecular layer deposition (MLD) has seen increased interest in recent years for the deposition of organic and hybrid organic-inorganic ultrathin films. This vapor-phase, layer-by-layer technique, which relies on the same self-limiting precursor saturation as atomic layer deposition, has shown promise for the development of many applications that require conformal organic-containing coatings, such as in photoresists, porous catalysts, and metal organic frameworks. Despite recent developments in MLD, there is a significant gap in our understanding of the mechanisms behind MLD and the microscopic properties of MLD-grown films, such as their molecular-level structure or degradation mechanisms. In this presentation, we will present results of our recent studies to understand such mechanisms, and discuss how that understanding can be used to better control the thermal, mechanical, electrical, and catalytic properties of these materials.

First, we discuss our exploration of the growth behavior of organic MLD films by examining trends in film properties as a function of backbone flexibility [1]. Our results suggest that changes in growth rate between the most rigid and most flexible backbones (4 Å/cycle vs 1 Å/cycle) are not caused by differences in length of molecular precursors, chain orientation (~25° on average for each backbone), or film density (1.0 – 1.2 g/cm$^3$), but are instead caused by an increased frequency of terminations in the more flexible chemistries. Because of the physisorption of precursors, which reintroduce reactive sites, these terminations do not lead a complete cessation of film growth. We further elaborate on the structure of the films by examining crystal orientation and infrared absorption data, which suggest that films consist of a mixture of upward growing chains and horizontally aligned layers of paracrystalline polymer segments.

Second, we discuss manganese/ethylene glycol hybrid films, which have promise as nanostructured, earth-abundant catalysts for electrochemical water splitting. Time-dependent ellipsometry, infrared absorption, and x-ray photoelectron spectroscopy data indicate that the organic component of the films is unstable in air, as seen in other hybrid MLD materials. The degradation pathway will be discussed, based on the observation that the organic linkers primarily degrade into carboxylate ions. Thermal annealing and chemical treatments, such as exposure to oxygen and water, are further shown to affect this degradation and can be used to control the formation of nanoporous, catalytically active catalysts for the oxygen reduction reaction.

1. D. S. Bergsman, et. al., Chem. Mater, 2017, 29, 1192

2:40pm **TF-MoA4 Inorganic Modification of Cellulosic Fibers for Enhanced Oil Sorption Capacity**, ***Andrew Short***, *S. Pamidi, Z. Bloomberg, M.D. Losego*, Georgia Institute of Technology

A few atomic layer deposition (ALD) cycles of metal oxides onto cellulosic fibers is known to modify the fiber’s surface energy and make the fiber hydrophobic. In this research we use the trimethylaluminum-water chemistry to make cellulosic fibers highly hydrophobic (WCA ~160°) and oleophilic, transforming natural cotton into an ideal material for oil spill remediation. The ALD-treated cellulose floats on water for over 12 months and readily sorbs oil, whereas untreated cellulose preferentially sorbs water over oil (Figures 1 and 2). ALD-treated cellulose has a significantly higher oil sorption capacity (e.g., 20 g g$^{-1}$ vs. 0.11 g g$^{-1}$) than raw cotton across a range of experimental conditions approximating those encountered in real-world oil spill remediation efforts (Figure 3). While studies in the literature report ultra-high oil sorption capacities (~200 g g$^{-1}$), this study finds that reporting oil sorption capacity in terms of g g$^{-1}$ can be misleading, and recommends this measure be reported in tandem with the material’s volumetric oil sorption capacity (g cm$^{-3}$) because of its greater relevance to use-case effectiveness. The comparison of g g$^{-1}$ and g cm$^{-3}$ oil sorption capacities given in Table 1 demonstrate that the sorbent produced here is comparable to some of the best reports in the literature. This talk will detail how the oil sorption capacity of these new materials change with differing real-world conditions and explain the efficacy of $Al_2O_3$ ALD applied to cellulosic fibers as a scalable, cost-effective method for creating biodegradable, on-demand materials for oil spill remediation.

3:20pm **TF-MoA6 Atomic Layer Deposition of Nano-Coatings on Fabrics for Antibacterial Applications**, ***Renee Puvvada***, *M. Bellavia, T.A. Sulchek, M.D. Losego*, Georgia Institute of Technology

About 1.7 million Americans contract hospital-acquired infections every year resulting in 99,000 inadvertent deaths and an estimated $20 billion in healthcare costs. Here, we investigate the use of atomic layer deposition (ALD) to treat various fabrics (e.g., polyester, cotton, and blends) with antimicrobial inorganic materials to create unique antibacterial linens, scrubs, and hospital gowns. Our protocols include biological testing of the antibiotic performance of ALD-treated fabrics against DH5-α, a strain of *E. coli* that is engineered to be suitable for laboratory purposes. Antibacterial performance is tracked as a function of ALD cycle number at various deposition temperatures. Fabrics were exposed to *E. coli* and then incubated for 20 hours, after which cultures are serially diluted up to 7 times, spotted onto Petri dishes, and incubated for another 20 hours. Colony counting is then used to quantify antibiotic effectiveness.

For ZnO ALD coatings of 0, 1, 10, and 100 cycles, we find that only the 100 cycle sample is sufficiently cytotoxic to kill all of the E. colibacteria. Interestingly, for only a few cycles of ZnO (1, 3, and 10 cycles) the bacteria appears to grow more rapidly. We attribute this increased bacterial growth

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*** TFD James Harper Award Finalist**

rate to the $Zn^{2+}$ ions acting as a nutrient for the bacteria. It is known that in order to be an effective antimicrobial agent, ZnO must be “nano-sized” or larger; atomic forms of Zn and ZnO, which ionize into $Zn^{2+}$ in nutrient broth, act instead as nutrients. A more detailed investigation of this transition from nutrient to antimicrobial will be discussed during this talk. We will also examine the effectiveness of other oxide materials including $TiO_2$ and $ZrO_2$ as well as compare the long-term performance of ZnO against common disinfectants like Lysol® and their stability in aqueous environments of varying pH.

### 4:00pm **TF-MoA8 ALD-based Functionalization of Biomaterials: Recent Developments and Future Challenges**, ***Christos Takoudis***, University of Illinois at Chicago **INVITED**

Biomaterials are engineered to interact with biological systems for therapeutic and diagnostic clinical applications. Biomaterials can be synthesized in a lab or can directly be obtained from natural resources, and they constitute whole or part of a biomedical device or a living structure that can be utilized to execute, improve, enhance or restore a natural function. The surface of a biomaterial controls the interactions occurring at the interface between the biomaterial surface and its surrounding living environment. Hence, successful performance of a biomaterial relies on its appropriate surface properties. Many biomaterials do not have appropriate surface functions and properties to cater to specific needs and applications. Therefore, surface modification and functionalization leading to significantly improved performance of biomaterials would be highly desirable and sought after.

In modern surface science and engineering, bio-nanotechnology is a potent tool to functionalize surfaces incorporating nanometer size thin films and nano-structural features into materials. Among the available deposition techniques, atomic layer deposition (ALD) offers unique advantages in yielding conformal thin films of metal oxides or metals (from a few Å to hundreds of nm thick), uniformly, with precise control at atomic or molecular level; in this manner, the performance and functionality of functionalized biomaterials could be selectively altered, optimized and controlled as needed.

ALD is a relatively new technique for optimizing materials in bio-nanotechnology. Here, after a brief review of the more widely used modes of ALD, ALD’s potential in bio-nanotechnology is presented with a few of its latest developments in biotechnology. ALD is promising means in tuning the hydrophilicity/hydrophobicity characteristics of biomedical surfaces, forming conformal ultra-thin coatings with desirable properties on high aspect ratio biomedical substrates, tuning the anti-bacterial properties of substrates surfaces of interest, and yielding multifunctional biomaterials for medical implants and other devices.

Recent developments on ALD at low (room or near room) temperature to functionalize the surface of heat-sensitive biomaterials with complex nanostructures are presented and discussed. Surface characterizations are done to investigate the morphology, chemical composition, crystallinity and wetting behavior of ALD-nanofilm coated biomaterial surfaces. The bioactivity of ALD $TiO_2$-coated surfaces, for example, is presented using in-vitro and in-vivo biocompatibility and biomineralization studies. Future challenges of ALD-based functionalization of biomaterials will be discussed.

### 4:40pm **TF-MoA10 Titanium Nitride ALD using Ultra-high Purity Hydrazine at Low Temperature**, ***Dan Alvarez***, *J. Spiegelman, R. Holmes, S. Allanson,* RASIRC, *A.C. Kummel, S. Wolf, M. Kavrik,* University of California, San Diego, *K. Andachi*, RASIRC

Overview

New channel materials such as SiGe, Ge and InGaAs create challenging thermal budgets (<400°C) for metal nitride deposition. TiNx metal gate electrodes in particular need new low temperature ALD methods.

Hydrazine has shown viable reactivity in previous studies but practical use has been limited due to purity concerns, especially water contamination [1-3]. Commercially available anhydrous hydrazine typically has a water concentration ranging from 0.2-2.0%. In addition to this low purity issue, oxygen concentration in metal-nitride films made using hydrazine is a high 4-15% for SiNx and TiNx.

Previous reports detail the safe delivery of gaseous hydrazine using a solvent-based formulation and membrane delivery system [4]. This presentation details studies on water measurement and removal, plus low resistivity films resulting from hydrazine-based low temperature TiNx ALD.

Hydrazine Purification, Measurement

Studies show that water contamination levels can be reduced to <50 parts-per-million (ppm) using new hydrazine source purification methods as measured by Karl-Fischer and GC-MS methods. Gas phase output of the ultra-dry materials was measured below the FT-IR moisture measurement method lower detection limit of 0.83ppm (Figure 1). Standard commercially available hydrazine has a comparatively high gas phase moisture measurement of 31ppm.

Titanium Nitride Deposition

Sequential pulsing of TiCl4 and N2H4 precursors at substrate temperatures of 275°C-350°C achieved atomic layer deposition TiNx. Initial measured resistivity at 350°C was a low $R_{average} = 130$ ohm, $R_{sheet} = 50$ ohm. Growth rate is approximately 0.5A per cycle. Films were characterized by XPS (Figure 2), AFM, KPFM, TEM and four-point sheet resistance. Little to no oxygen was present in the TiNx film, which had a near stoichiometric ratio of Ti/N. The presentation will include additional optimization to reduce residual chlorine content at lower temperatures. In addition, a correlation with regards to residual Chlorine content/Resistivity versus deposition temperature will be discussed.

**References**

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### 5:00pm **TF-MoA11 ALD Barriers for Protection of Electronic Devices in Biological Environment**, ***Ankit Singh***, *K. Adstedt, S. Graham*, Georgia Institute of Technology

Encapsulation plays a significant role in the protection and lifetime enhancement of electronic devices. Devices like OPVs, OLEDs, biological implants, and thin film solar cells are susceptible to rapid degradation on exposure to the surrounding media containing moisture and ionic species. Encapsulation barriers hermetically seal the devices and thus, prevent the ingress of moisture or any other fluid that can affect the function and stability of the devices. It involves use of inorganic barrier layers deposited using vacuum deposition processes. Out of several vacuum deposition techniques used for this purpose, atomic layer deposition (ALD) has shown an outstanding performance by producing films which have water vapor transmission rate less than $10^{-4}$ $g/m^2/day$. However, the performance and reliability of ALD barrier films is subject to their stability and resistance to corrosion in the surrounding environment.

Recently, miniaturized medical devices have gained popularity because of their new treatment and monitoring capabilities, ease of application and enhanced portability. These devices include artificial pacemakers, cochlear implants, artificial heart valves, etc. These devices are exposed to different bodily fluids that have varying pH and salt concentrations. Any electronic device cannot be expected to last for long enough time to be used as an implant with any protective covering. Thus, it becomes imperative to look for a robust solution.

In this work, we explore the use of different metal oxides deposited using ALD at 100°C in biological environment. The materials include $Al_2O_3$, $HfO_2$, $TiO_2$ and $ZrO_2$. Chemical stability of the ALD films is determined by using electrochemical impedance spectroscopy (EIS) whereas, biocompatibility of the ALD films is determined using MTT cell proliferation assay measurements. For chemical stability test using EIS, a 3 electrode setup was used to understand the mechanism of material degradation. The ALD deposited materials were exposed to phosphate buffer saline (PBS) solution, simulated sweat and saliva, and Dulbecco's Modified Eagle Medium (DMEM) for 21 days. Besides ALD $Al_2O_3$, other metal oxides have demonstrated enhanced corrosion resistance and stability in different solutions. ALD $HfO_2$ has better stability as compared to ALD $Al_2O_3$ but tends to develop crack with long exposure time. However, ALD $TiO_2$ and $ZrO_2$ were found to be most stable in all the biological solutions used for testing. All the ALD materials used during the test have been found to be biocompatible using MTT cell proliferation test. Finally, we demonstrate the application of these ALD materials for protection of active implantable devices.

## Tandem MS Focus Topic
## Room: 5 & 6 - Session TM-MoA

## Applications in Mass Spectrometry Imaging using Tandem MS
**Moderators:** Gregory L. Fisher, Physical Electronics, Alexander Pirkl, ION-TOF GmbH, Germany

2:40pm **TM-MoA4 Utilization of Complementary Multimodal Techniques for *in situ* Identification of Soybean Root Nodule Metabolites**, *S. Stopka,* The George Washington University*, D. Veličković,* Pacific Northwest National Laboratory, *B. Agtuca,* University of Missouri, *D.W. Koppenaal, L. Paša-Tolić,* Pacific Northwest National Laboratory, *G. Stacey,* University of Missouri, *A. Vertes,* The George Washington University, ***Christopher R. Anderton***, Pacific Northwest National Laboratory

In an effort to attain more sustainable agricultural practices, there is a great interest in understanding metabolic processes within plant systems known to acquire nitrogen through biological nitrogen fixation. The symbiotic association between nitrogen-fixing soil bacteria (*Rhizobiaceae*) and plants of the family *Leguminosae* are one such system of interest. This symbiosis generates specialized organs, called root nodules, where rhizobia reduce $N_2$ into bioavailable products accessible to the host plant, and in exchange the plant provides a carbon source to the bacteria to ensure (among other things) sufficient energy for nitrogen fixation. Using both laser ablation electrospray ionization (LAESI) and matrix-assisted laser desorption/ionization (MALDI) mass spectrometry (MS) methods, we explored the array of metabolites involved, and their spatial distribution, that influence the rhizobia-legume association of *Bradyrhizobium japonicum* and soybean (*Glycine max* Williams 82). While these MS-based spatial metabolomics approaches provided insight into the heterogeneous distribution of analytes within soybean root nodules, orthogonal measurements were required for increased levels of confidence in the molecular identifications of the detected species. Here, we will describe how tandem MS, pre-mass analysis ion mobility separations, and high mass resolution and mass accuracy measurements of the isotopic envelope were utilized to provide confidence in the identity and localization of metabolites within soybean root nodules. We further applied this information to elucidate active metabolic pathways within different compartments of the nodules.

3:00pm **TM-MoA5 Coupling Front-end Electron Transfer Dissociation to Ultra-High Field FTICR-MS**, ***Chad Weisbrod****, D.F. Smith, L.C. Anderson, L. He, A.G. Marshall, C.L. Hendrickson*, The National High Magnetic Field Laboratory **INVITED**

Tandem MS is an indispensable tool of the mass spectrometrist. It enables structural elucidation and aides in unambiguous identification of precursor ions. Many means of performing tandem MS exist and can largely be categorized into three distinct groups: collision-, electron-, and photon-based. Each group has its own set of analytical merits and must be considered carefully when choosing which will best suit the analytical demand. Further, tandem MS can occur in-space or in-time which are unique to specific mass spectrometer configurations. A brief discussion of these categories of tandem MS will be given along with their relative strengths and weaknesses. A justification for our incorporation of front-end electron transfer dissociation (FETD) within the 21 T FTICR-MS at NHMFL will also be discussed. The 21T FT ICR-MS at NHMFL was constructed to achieve extraordinary performance with respect to top-down analysis. This is achieved by the increased field strength and the culmination of several technologies included during its construction. Here we focus on the inclusion of front-end electron transfer dissociation (FETD) coupled with an external multipole storage device (MSD), which allows for analysis of larger cumulative ion targets than ever before and lessens the need transient summing. We demonstrate linear operational range in terms of cumulative ion target (<5.0E4-3E7 total charges) and mass spectra with very high sequence coverage, in-spectrum dynamic range, and mass measurement accuracy despite the large cumulative injection targets. We show performance of FETD applied to standard proteins (3-30 kDa), human cell lysate samples, and monoclonal antibodies.

## Vacuum Technology Division
## Room: 7 & 8 - Session VT-MoA

## Material Outgassing, Adsorption/Desorption and XHV
**Moderators:** Giulia Lanza, SLAC National Accelerator Laboratory, Jacob Ricker, NIST

1:40pm **VT-MoA1 Weight of Water on the Solid Surface in Air and Vacuum**, ***Richard Green***, National Research Council of Canada, Canada **INVITED**

In 2018, after over 30 years of research by national measurement laboratories around the globe, the unit Kilogram is expected to be redefined in terms of a fundamental constant of nature; Planck's constant. The present definition has not significantly changed in over 120 years and relates to a single cylinder made of exactly one kilogram of platinum-iridium alloy that is stored in a vault in Sèvres, France. In order to connect the present Kilogram measured in air to a redefined Kilogram measured in vacuum, new tools and methodologies have been developed to understand and quantitatively determine the change in mass that occurs when metals are placed in vacuum. While initially concerned with platinum, work has extended to stainless steel and other surfaces. With resolutions on the order of a 100 parts per trillion possible, sorption of less than 0.01 monolayers of water is observable.

In this talk we will present measurement techniques and tools used to quantitatively and traceably determine the weight of water and hydrocarbons desorbed from a surface as it is exposed to vacuum. The techniques have been used to study factors such as pressure, surface roughness and contamination, which influence the quantity and dynamics of desorbed mass. The investigations will be presented in context of efforts at the National Research Council of Canada to make the world's most accurate measurement of Planck's constant.

2:20pm **VT-MoA3 Hydrogen Measurement using a Thermal Desorption Spectrometer**, ***JongYeon Lim***, Korea Research Institute of Standards and Science, Republic of Korea, *K.D. Kim, H.S. Oh, C.H. Lim, Y.D. Joh*, Infinity Vacuum Technology, Republic of Korea

The TDS system, designed for measuring outgassing rate of a diameter of 10 mm sample, with two pumping paths; one is ordinary throughput path with an orifice, the other a UHV path, has been newly developed to measure any molecules on samples with a sophisticated DAQ system.

Two paths are directly connected to the main chamber equipped with devices including a rod-guided halogen heater allowing the sample temperature up to 1200 $^{o}$C .

The throughput path utilizes the UHV equipment to measure the outgassing rate quantitatively and qualitatively. In the case of quantitative hydrogen measurement, the throughput path does not have enough pumping speed since a small orifice diameter has the conductance limitation.

The experimentally acquired system calibration factor for the throughput method is 16.0, which is defined as the ratio of background outgassing rates with the gate valve closed and open using the throughput method.

In order to verify the measurement reliability a NIST Standard Reference Materials (SRM) was introduced to the TDS system. Most of hydrogen was desorbed during the course of heating process up to 800 $^{o}$C for 90 minutes. The area under the H2 peak is proportional to the nominal value of 126.8 wt ppm (uncertainty of 2 %). The hydrogen calibration factor of 4.38686E23 was realized. The system claims the hydrogen measurement resolution of 1.3E-6 wt ppm.

In this presentation we briefly introduce the accurate UHV outgassing measurement system for both qualitative and quantitative analyses, which has an 18 % uncertainty of total outgassing rate with Inficon BPG400 HV gauges and a unique self-calibration function.

*Acknowledgements: Results are partially attributed to two national projects sponsored by the Korean Ministry of Trade, Industry & Energy, and the KRISS main project (Contract Nos. 10048806, and 170111649).*

2:40pm **VT-MoA4 Automatic Flowmeter and Dynamic Expansion System for UHV/XHV Studies**, ***James Fedchak****, J. Scherschligt, D. Barker, S. Eckel*, NIST

NIST is presently creating the Cold Atom Vacuum Standard (CAVS), a quantum-based fundamental primary vacuum sensor which significantly departs from present methods of measuring and realizing ultra-high vacuum (UHV) and extreme-high vacuum (XHV). The CAVS is an absolute sensor based on the loss-rate of ultra-cold atoms from a conservative magnetic trap due to collisions of the trapped cold atoms with the ambient background gas, and will cover a pressure range of $10^{-8}$ torr to below $10^{-12}$ torr, thus spanning UHV and into XHV. Knowledge of the thermalized collision cross-section, or loss-rate coefficient, between the trapped ultra-cold sensor atoms and the background gas is critical to operation of the CAVS; such collisions are also important in other experiments and devices based on trapped cold atoms because they limit the lifetime of atoms in the trap and, in addition, glancing collisions can increase statistical and other uncertainties. To support the CAVS and other atomic physics programs, NIST is developing a dynamic expansion system to set a known pressure in the CAVS, which will allow the experimental determination of collision cross-sections, relative gas-sensitivity factors, and facilitate studies of other systematic effects. To that end, we are developing a constant pressure flowmeter capable of producing flows of at least $10^{-13}$ mol/s and a dynamic expansion system to produce pressure rises as small as $10^{-10}$ Pa. The system is designed to produce low gas-flows of $H_2$ and many other gases of interest, to be fully automated, and to have extremely low outgassing rates. The design and construction of the UHV/XHV flowmeter and dynamic expansion system will be discussed.

3:00pm **VT-MoA5 Development of a New UHV/XHV Pressure Standard (Cold Atom Vacuum Standard)**, ***Julia Scherschligt***, *J.A. Fedchak, S. Eckel, D. Barker*, NIST **INVITED**

NIST has a long history of laser cooling and trapping of neutral atoms, largely motivated by building better time standards or clocks, and has recently begun a program to extend the metrological capabilities of cold trapped atoms to measurement of vacuum. This will align vacuum metrology to the emergent NIST "Quantum SI" paradigm, in which a measurement has intrinsic traceability and the line between sensor and standard is blurred. Since the earliest days of neutral atom trapping it has been known that the background gas in the vacuum limits the lifetime of atoms in the trap. We are inverting this problem to create a quantum-based standard and sensor. Indeed, because the measured loss-rate of ultra-cold atoms from the trap depends on a fundamental atomic property (the loss-rate coefficient or thermalized cross section) such atoms can be used as an *absolute* sensor and *primary* vacuum standard. Researchers have often observed that the relationship between the trap lifetime and background gas can be an indication of the vacuum level, but a true absolute sensor of vacuum has not yet been realized. This is because there are many technical challenges that must be overcome to create a device that's truly absolute and primary. The NIST program addresses these challenges both theoretically and experimentally: we have begun *ab initio* calculations of collision cross sections between the trapped cold atoms and the background gas and, on the experimental side, we are thoroughly investigating the systematic uncertainties associated with using an atom trap to determine vacuum level, particularly those associated with loss mechanisms (in a non-ideal trap) other than due to background collisions. We are designing and building the apparatus to measure relevant cross sections, and building our first prototype vacuum sensing apparatus. In this presentation, we will discuss our theory progress, and present our newest measurements, as well as discuss how the Cold Atom Vacuum Standard fits into the broader picture of the NIST dissemination of the Quantum SI.

4:00pm **VT-MoA8 VTD Early Career Award Invited Talk: Modern Metrology Practice for Calibration and Reliability Testing of Vacuum Measurement Products**, ***Scott Heinbuch****, MKS Instruments, Inc. **INVITED**

Vacuum technology is traditionally very slow moving in terms of new techniques and innovations. The measurement techniques of today don't differ drastically from 20 years ago or even longer. That does not mean there aren't new ways we can think about how we use that measurement technology in a metrology lab today. Often times, critical vacuum measurements take time; time being a taboo word in today's product development discussions. There are many practices to help us reduce time waste while still ensuring good vacuum measurement. Principles of Lean have helped us to reduce types of waste in our lab creating an efficient environment where experiments can be set up accurately and timely. Similarly, Six Sigma ideas have given us a set of tools and a common language to quickly identify root cause for problems and simplify our data analysis techniques. These same tools have helped us to identify critical parameters for measurement systems analysis and better understanding of our measurement uncertainties when making measurements compared to our best in class Spinning Rotor, Stabil-Ion®, and Baratron® reference transducers. To further simplify our lab experience, vacuum system complexity has been reduced by an effort to separate the vacuum control system from our test development in which any user can interface with a vacuum system in the same way they would interface with a common laboratory instrument whether manually, or through a programming interface. Finally, none of this matters unless we are making our measurements with our customers in mind. Several customer applications have been reproduced and turned into standard tests for our products to improve our customers experience and our overall product performance and reliability.

4:40pm **VT-MoA10 Outgassing Rate Measurements of New Materials at NIST**, ***Makfir Sefa***, *J.A. Fedchak, J. Scherschligt, A. Zeeshan*, NIST

The Thermodynamic Metrology Group at NIST is interested in investigating the outgassing rates and gas uptake properties of a variety of materials. The motivation of these investigations is to support programs aimed to develop new vacuum, pressure, and temperature sensors. For example, materials with ultra-low outgassing rates are necessary to develop a cold-atom vacuum standard (CAVS), which is a metrological-quality XHV/UHV sensor based on ultra-cold atom technology. Chambers and vacuum components used in the CAVS must have ultra-low outgassing rates to achieve UHV and XHV backgrounds. The group is also interested in developing embedded temperature and pressure sensors, where the outgassing or gas uptake properties could influence sensor performance or applicability. In addition, the gas uptake properties of unique materials can be exploited for gas sensors or storage. This talk will highlight the outgassing measurements of heat-treated stainless steel chambers and 3-D printed stainless steel and titanium chambers. In addition, absorption and desorption of gases in 3-D printed nano-composite plastics will be discussed.

5:00pm **VT-MoA11 Scaling up an Ion Implant Process Chamber Cryopumping for 450mm Wafer Processing**, ***Steve Borichevsky***, Applied Materials, Varian Semiconductor Equipment

The semiconductor industry recently explored scaling up the wafer diameter from 300mm to 450mm. Ion Implant faced the challenge of providing process vacuum conditions for larger dopant ion beam currents and coping with the outgassing cause by the ion beam striking increased area covered by photoresist. The process chamber, where the ion beam strikes the target wafer, posed the most difficult vacuum challenges. The increased wafer size was predicted to generate 2.25 times the normal gas loads which would require nine 320mm cryopumps. In order to meet the requirements of implant, three prototype 500 mm diameter cryopumps were mounted onto a process chamber and tested. This presentation describes the basic architecture of an ion implanter, the decisions that lead up to the use of 500mm cryopumps, the results of the initial vacuum system testing and the Monte Carlo simulations.

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*** VTD Early Career Award**

## Plenary Session
## Room: Ballroom B - Session PLS-MoPL

### Plenary Session

5:30pm **PLS-MoPL1 Precise Chemical, Physical, and Electronic Nanoscale Contacts**, ***Paul Weiss***, University of California at Los Angeles **INVITED**

The physical, electronic, mechanical, and chemical connections that materials make to one another and to the outside world are critical. Just as the properties and applications of conventional semiconductor devices depend on these contacts, so do nanomaterials, many nanoscale measurements, and devices of the future. We discuss the important roles that these contacts can play in preserving key transport and other properties. Initial nanoscale connections and measurements guide the path to future opportunities and challenges ahead. Band alignment and minimally disruptive connections are both targets and can be characterized in both experiment and theory. I discuss our initial forays into this area in a number of materials systems.

Paul S. Weiss holds a UC Presidential Chair and is a distinguished professor of chemistry & biochemistry and of materials science & engineering at UCLA. He received his S.B. and S.M. degrees in chemistry from MIT in 1980 and his Ph.D. in chemistry from the University of California at Berkeley in 1986. He was a postdoctoral member of technical staff at Bell Laboratories from 1986-88 and a visiting scientist at IBM Almaden Research Center from 1988-89. He served as the director of the California NanoSystems Institute and held the Fred Kavli Chair in NanoSystems Sciences at UCLA from 2009-14. Before coming to UCLA, he was a distinguished professor of chemistry and physics at the Pennsylvania State University, where he began his academic career in 1989. His interdisciplinary research group includes chemists, physicists, biologists, materials scientists, mathematicians, electrical and mechanical engineers, computer scientists, clinicians, and physician scientists. They focus on the ultimate limits of miniaturization, exploring the atomic-scale chemical, physical, optical, mechanical, and electronic properties of surfaces, interfaces, and supramolecular assemblies. He and his students have developed new techniques to expand the applicability and chemical specificity of scanning probe microscopies. They have applied these and other tools to the study of catalysis, self- and directed assembly, and molecular and nanoscale devices. They advance nanofabrication down to ever smaller scales and greater chemical specificity in order to operate and to test functional molecular assemblies, and to connect these to the biological and chemical worlds. Two major themes in his laboratory are cooperativity in functional molecules and single-molecule/assembly biological structural and functional measurements. He has written over 300 publications, holds over 30 patents, and has given over 600 invited, plenary, keynote, and named lectures.

Weiss has been awarded a National Science Foundation (NSF) Presidential Young Investigator Award (1991-96), the Scanning Microscopy International Presidential Scholarship (1994), the B. F. Goodrich Collegiate Inventors Award (1994), an Alfred P. Sloan Foundation Fellowship (1995-97), the American Chemical Society (ACS) Nobel Laureate Signature Award for Graduate Education in Chemistry (1996), a John Simon Guggenheim Memorial Foundation Fellowship (1997), a NSF Creativity Award (1997-99), and the ACS Award in Colloid and Surface Chemistry (2015), among others. He was elected a fellow of: the American Association for the Advancement of Science (2000), the American Physical Society (2002), the American Vacuum Society (2007), the ACS (2010), the American Academy of Arts and Sciences (2014), the American Institute for Medical and Biological Engineering (2016), and an honorary fellow of the Chinese Chemical Society (2010). He was also elected a senior member of the IEEE (2009). He received Penn State's University Teaching Award from the Schreyer Honors College (2004), was named one of two nanofabrication fellows at Penn State (2005), and won the Alpha Chi Sigma Outstanding Professor Award (2007). He was a visiting professor at the University of Washington, Department of Molecular Biotechnology (1996-97) and Kyoto University, Electronic Science and Engineering Department and Venture Business Laboratory (1998 and 2000), and a distinguished visiting professor at the Kavli Nanoscience Institute and the Joint Center for Artificial Photosynthesis at Caltech (2015). He is a visiting scholar at the Kavli Institute for Bionano Science & Technology and the Wyss Institute for Biologically Inspired Engineering at Harvard University (2015-17). He has been named the Institut National de la Recherche Scientifique (INRS) Chaire d'excellence JacquesBeaulieu at the Centre for Energy, Materials and Telecommunications (2016-17). Weiss was a member of the U.S. National Committee to the International Union of Pure and Applied Chemistry (2000-05). He has been the technical co-chair of the Foundations of Nanoscience Meetings, thematic chair of the Spring 2009 and Fall 2018 ACS National Meetings. He was the senior editor of IEEE Electron Device Letters for molecular and organic electronics (2005-07), and is the founding editor-in-chief of ACS Nano (2007-). At ACS Nano, he won the Association of American Publishers, Professional Scholarly Publishing PROSE Award for 2008, Best New Journal in Science, Technology, and Medicine, and ISI's Rising Star Award a record ten times.

## 2D Materials Focus Topic
## Room: 15 - Session 2D+AS+SA+SP-TuM

### 2D Materials Characterization including Microscopy and Spectroscopy
**Moderator:** Sara Barja, Materials Physics Center, San Sebastián, Spain

8:00am **2D+AS+SA+SP-TuM1 Electronic Structure of Oxygen-Intercalated Graphene on Iridium Interface**, ***Yi Lin***, *Y. Li,* Columbia University, *J. Sadowski,* Brookhaven National Laboratory, *J. Dadap, W. Jin, R. Osgood,* Columbia University, *M.S. Hybertsen*, Brookhaven National Laboratory

We report experimental and theoretical work to understand how oxygen intercalation changes the image potential state and surface state electronic structure in a metal/graphene interface. We use tunable angle-resolved two-photon photoemission spectroscopy to probe the evolution of the electronic band structure of an epitaxially grown monolayer graphene on Ir(111) as it undergoes through a cycle involving oxygen intercalation and deintercalation. Oxygen intercalation is carried out in situ and LEED is used to determine the crystallinity of the interface in the presence or absence of the intercalated oxygen. The image state manifold and its effective mass are examined. The photoemission intensity variation in momentum space and the observation of an oxygen induced state are discussed. Furthermore, a recently proposed effective potential model at the graphene/metal interface is developed further by us to accommodate oxygen intercalation and interpret our experimental electronic structure variation with good agreements.

We acknowledge support from the US Dept. of Energy, Office of Basic Energy Sciences, under Contract Numbers DE-FG 02-04-ER-46157, DE-FG02-90ER14104, and DESC0012704.

8:20am **2D+AS+SA+SP-TuM2 Graphene Moiré Pattern Ultra-High Resolution Atomic Force Microscopy**, ***Gerald Pascual***, *B. Kim, K. Lee,* Park Systems Inc.

The ultra-high resolution of AFM was demonstrated in a Graphene/hexagonal Boron Nitride (hBN) sample evaluation conducted by AFM. The sample consisted of hBN substrate overlaid with a Graphene layer and was scanned under ambient air. The purpose of the evaluation was to assess the AFM ability to characterize the topography of the moiré pattern that was created when one layer was set on top of the other and offset by rotation. Using non-contact AFM mode and a standard AFM probe tip, the AFM was able to successfully image the moiré pattern super lattice constant of the sample in scans as large as 500 x 500 nm. In the higher magnification image taken at a scan size of 60 x 60 nm provides the clear evidence that not only are the super lattice constants of the moiré pattern about 15 nm [1] in width, but that the spacing between each striation on the moiré pattern is roughly 4-5 nm in length. Observations of such striations in Graphene/hBN systems have been previously reported [2]. This latter distance is in line with the expected tip radius curvature values for the AFM tip used to acquire all four sets of data.

[1] A. Zandiatashbar, B. Kim, Y. Yoo, and K. Lee, Microscopy Today 23(06):26-31 (2015)

[2] P. Gallagher, M. Lee, F. Amet et.al., Nature Comm. 7 10745 (2016)

8:40am **2D+AS+SA+SP-TuM3 Surface and Interface Properties of 2D $MoS_2$ and $WS_2$ Materials**, ***Chia-Seng Chang***, Institute of Physics, Academia Sinica, Taiwan, Republic of China, *Y.H. Lee*, National Tsing-Hua University, Taiwan, Republic of China **INVITED**

Two dimensional layered transition metal dichalcogenides (2D TMD), such as $MX_2$ (M = Mo, W and X = S, Se), have offered exciting new physics and chemistry, as well as potential applications in energy harvesting, electronics, and optoelectronics. Surface and interface properties of these 2D materials are fundamental to further advance them on scientific exploration and device fabrication. In this talk, we will demonstrate the growth of various TMD monolayers using ambient-pressure chemical vapor deposition. The quality of a $MS_2$ monolayer was examined by scanning probe microscopy, electron microscopy, and optical spectroscopy. We will discuss the key issues associated with the surfaces and interfaces of these materials.

9:20am **2D+AS+SA+SP-TuM5 Spectroscopic Investigation of Plasma-Fluorinated Monolayer Graphene and Application for Gas Sensing**, ***Hui Zhang***, Shanghai Institute of Microsystem And Information Technology, China, *J.-H. Guo,* Lawrence Berkeley National Laboratory, *X. Sun*, Soochow University

A large-area monolayer fluorinated graphene (FG) is synthesized by a controllable SF6 plasma treatment. The functional groups of FG are elucidated by various spectroscopies, including Raman, X-ray photoemission spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS). Raman results suggest that the defects are introduced into the monolayer graphene during the fluorination process. The fluorine content can be varied by the plasma treatment and can reach the maximum (~24.6 at% F) under 20 s plasma treatment as examined by XPS measurement. The angle dependent NEXAFS reveals that the fluorine atoms interact with the graphene matrix to form the covalent C-F bonds, which are perpendicular to the basal plane of FG. FG is applied as gas sensing material and owns much better performance for ammonia detection compared to the pristine graphene. Based on our DFT simulation results, the fast response/recovery behavior and high sensitivity of the FG gas sensor are attributed to enhanced physical absorption due to the C-F covalent bonds on the surface of FG

9:40am **2D+AS+SA+SP-TuM6 Photoemission Electron Microscopy as a New Tool to Study the Electronic Properties of 2D Crystals on Silicon Oxide**, ***Taisuke Ohta***, *M. Berg,* Sandia National Laboratories, Center for Integrated Nanotechnologies, *C. Chan,* Sandia National Laboratories, *K. Keyshar,* Rice University, *G. Gupta,* University of Louisville, *P. Ajayan,* Rice University, *A. Mohite*, Los Alamos National Laboratory

The energy positions of the valence and conduction electronic states with respect to the vacuum level are essential parameters to evaluate how the band gaps of semiconductors or Fermi-levels of metals would line up with respect to each other. Defined as an energy separation between the vacuum level and the highest occupied electronic states, the ionization energy is of particular importance for atomically-thin two-dimensional (2D) crystals to predict the performance of their heterostructures useful in high performance electronics and opto-electronics. Ionization energies have been investigated based on theoretical calculations, but to the best of our knowledge, no systematic experimental confirmation is reported for the wide range of 2D crystals despite their importance.

Here, we present a new approach to study the electronic properties of prototypical 2D crystals, graphene, $MoS_2$, $WS_2$, and $MoSe_2$ monolayer and multilayer flakes, supported on thick silicon oxide ($SiO_2$) film using a photoemission electron microscopy combined with a deep ultraviolet (DUV) illumination. We determine the band alignments of monolayer to multilayer junctions in these four materials, and show that the ionization energy decreases from $MoS_2$, $WS_2$, to $MoSe_2$ as predicted by density functional calculations. We postulate that the defects in $SiO_2$ alleviate the charging of the 2D crystals thanks to the relatively low total photoemission current due to the low energy excitation by the DUV light. This study reveals a new metrology to uncover electronic properties intrinsic to 2D crystals supported on $SiO_2$ substrates that interact minimally with the overlying 2D crystals.

The PEEM work was performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility (DE-AC04-94AL85000). T. O. is supported by the CINT user program and Sandia LDRD. The work performed by M. B. and C. C. are supported by a U.S. DOE, Office of Energy Efficiency and Renewable Energy SunShot Initiative award for BRIDGE (DE-FOA-0000654 CPS25859). K. K. was supported by the Army Research Office MURI grant W911NF-11-1-0362. A. D. M. is supported by LANL LDRD program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

11:00am **2D+AS+SA+SP-TuM10 STM and STS Study of $MoS_2$/$WS_2$ Heterostructures Grown by Chemical Vapor Deposition**, ***Fan Zhang***, Virginia Polytechnic Institute and State University, *Z. Lu,* Tsinghua University, PR China, *H. Zheng, K. Park,* Virginia Polytechnic Institute and State University, *L. Jiao,* Tsinghua University, PR China, *C. Tao*, Virginia Polytechnic Institute and State University

2D materials like atomically thin transition metal dichalcogenides (TMDs) have received tremendous attentions for their unique properties and high potential applications. Recent developments on synthesis of 2D heterosrtuctures through the chemical vapor deposition (CVD) method provide an unprecedented opportunity to create and tune the intriguing electronic and optical properties of 2D materials such as engineering the band gaps. These 2D heterostructrues have a wide range of applications in electronics and optics, for example, tunneling transistors, single-photon emission devices and photovoltaic devices. To further optimize and design 2D heterostructures, it is essential to investigate the structural and electronic properties at the atomic scale, which is however still lacking.

In this presentation, we will focus on a high-quality $MoS_2/WS_2$ heterostructure grown on $SiO_2$ using the CVD method. Scanning tunneling microscopy (STM) and spectroscopy (STS) were performed to study the morphology and band structures of both $MoS_2$ monolayer and $MoS_2/WS_2$ heterobilayer. Atomically resolved STM images were obtained on the monolayer, heterobilayer and the interface between the monolayer and heterobilayer. The height histograms acquired respectively on the monolayer and the heterobilayer indicate that the heterobilayer is higher than the monolayer with a height difference of $0.85 \pm 0.10$ nm. The roughness of the monolayer and heterobilayer was for the first time quantified by STM. The root mean square (RMS) roughness of the heterobilayer is $0.253 \pm 0.020$ nm compared with $0.362 \pm 0.031$ nm of the monolayer. We also performed STS measurements on the system. Our STS results and density functional theory (DFT) calculations reveal the band gaps of the heterobilayer and the $MoS_2$ monolayer, which are similar to the previously reported results on $MoS_2/WS_2$ heterostructures fabricated through the mechanical exfoliation method.

11:20am **2D+AS+SA+SP-TuM11 Determine the Band Alignment of 2D Semiconductor Heterostructures by Photoelectron Spectromicriscopy**, *L.Y. Chang*, National Synchrotron Radiation Research Center, Taiwan, Republic of China, *Y.-X. Wang, Y.-H. Ku*, National Tsing Hua University, Republic of China, *Y.-C. Kuo, H.-W. Shiu,* ***Chia-Hao Chen***, National Synchrotron Radiation Research Center, Taiwan, Republic of China

Semiconductor heterojunction (HJ) band alignment is the most important factor for the functioning of the HJ-based devices. Therefore, the prediction and determination of the HJ band offset is always a scientifically interesting and technologically important topic. As the 2D materials emerged as the building blocks for the devices with molecular thickness, the determination of band alignment of the van der Waals HJs is becoming a critical issue.

Due to the nature of the molecular thickness and the lack of large area 2D crystal, a microscope with surface sensitivity is an ideal tool to study the fundamental properties of the 2D heterostructures.

In this regard, we have employed a synchrotron radiation based scanning photoelectron spectromicroscopy (SPEM) to study the chemical and electronic structures of the van der Waals HJs, include the single-layer transition metal dichalcogenides, and graphene/GaN HJs. In this presentation, I will report some of the band alignments of these 2D semiconductor heterostructures.

## Actinides and Rare Earths Focus Topic
## Room: 22 - Session AC+AS+SA-TuM

## Nuclear Power, Forensics, and Other Applications
**Moderator:** James G. Tobin, University of Wisconsin-Oshkosh

8:00am **AC+AS+SA-TuM1 Design of Synergistic Protein-ligand Systems for f-element Coordination, where Separation, Decontamination and Nuclear Medicine Meet**, ***Rebecca Abergel***, Lawrence Berkeley National Laboratory **INVITED**

Separation of elements from the 4*f*- and 5*f*- series is a challenging task due to the similarities in their ionic radii and the existence of most of these metal ions in the trivalent oxidation state. Understanding the fundamental bonding interactions between those metal centers and selective ligands presents a rich set of scientific challenges and is critical to the development of new separation strategies as well as to a number of applied problems such as the need for decontamination after a nuclear accident or the use of radio-isotopes for new cancer treatments. Our studies utilize luminescence sensitization, UV-Visible, X-ray absorption, and X-ray diffraction spectroscopic techniques to investigate specific lanthanide and actinide coordination features by bio-inspired catecholamide and hydroxypyridinone hard oxygen-donor ligands. Using such ligands allows the solution differentiation of different metals through stabilization in specific oxidation states and provides information on their respective electronic structures. In addition, X-ray diffraction analyses using the mammalian iron transport protein siderocalin as a crystallization matrix revealed remarkable aspects of the protein's interactions with chelated metals, establishing series of isostructural systems that can be used to derive trends in the later 5*f*-element sequence, when combined with theoretical predictions. These results will be discussed with a perspective on how such studies have important implications for the use of spectroscopic and thermodynamic methods to exploit the fundamental knowledge of the role of *f*-electrons in actinide bonding for the development of new transport, separation, luminescence, and therapeutic applications.

8:40am **AC+AS+SA-TuM3 Image Processing And Particle Analysis Of Fission-Truck-Analysis In Nuclear Forensic**, ***Itzhak Halevy***, Department of Physics, NRCN, Israel, *U. Admon,* (Retiree), IAEC-NRCN, Department of Materials, Beer-Sheva Israel, *E. Chinea-Cano,* Office of Safeguards Analytical Services (SGAS), International Atomic Energy Agency (IAEA), Austria, *A.M. Weiss*, Faculty of Engineering, Bar-Ilan University, Israel, *N. Dzigal,* Office of Safeguards Analytical Services (SGAS), Austria, *E. Boblil*, Department of Physics, IAEC-NRCN, Israel

Particle analysis is a key discipline in safeguards and nuclear forensic investigations, as well as in environmental research. The radioactive Particles are usually in the micrometric size range, and intermixed within huge populations of other particles, like air-borne dust, soil, industrial exhaust pollutants or estuary sediments.

We are using the Fission Truck Analysis (FTA) technique. In that technique plastic detectors used for raping a Lexan catcher with the particles and together are radiated in nuclear reactor with thermal neutrons. The Fission Truck are trucks done by the fission products. The fission material is dominant in producing the trucks, namely the $^{235}$U isotope. The Fission Truck could be more visible by special etching and can be used to locate the particles.

From that point, the analysis of Fission Truck is an image processing. Scanning the detectors is a time-consuming procedure. Automated scanning and fission star recognition will make all the Analysis easier to quantify

The challenge, therefore, consists in scanning and imaging a relatively large area detector, at a resolution of about 1µm, and locating the FT clusters while rejecting the artefacts.

Image processing was done using the Fiji distribution of ImageJ. The algorithms shown in this report were implemented using either the ImageJ macro language or the ImageJ Python scripting engine. Basic noise removal, Illumination correction and Segmentation are the basic of the imaging analysis.

I cass of large area detector a set of picture will be taken and by stiching a larg picture will be composed.

Roundness and endpoint thresholds can be adjusted to obtain fewer false negatives at the expense of more false positives. A receiver operation characteristic (ROC) can be used to characterise this.

The high and low threshold determination in the hysteresis thresholding step should be improved.

After the autometed procedure the operator can go over the FT and decide if to add stars that were not found by the software or to cancel stars that are artifact.

Correlation between forensic and image processing parameters will be defined. Even that stars are coming from $^{235}$U only and it is no one to one connected only to enrichment we still think that the shape, color, number of end points and roundness can be parameters to indicates different forensic properties.

9:00am **AC+AS+SA-TuM4 Application of Linear Least Squares to the Analysis of AES Depth Profiles of Plutonium Oxides**, ***Scott Donald***, *A.J. Nelson*, Lawrence Livermore National Laboratory

Application of the linear least squares (LLS) methodology allows for quantitative determination of variation in material composition with depth, as well as permitting an understanding of differences resulting from changes in the method of preparation. LLS fits were applied to decompose and enhance the interpretation of spectra obtained by Auger electron spectroscopy (AES) during depth profiles of oxidized plutonium surfaces. By means of the LLS algorithm, chemical state assignments of the Pu $P_1VV/O_{45}VV$, O KLL, and C KLL Auger transitions were determined and the existence of a subsurface oxy-carbide layer was identified, with confirmation provided from comparison to previous measurements of standard samples.

The work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

9:20am **AC+AS+SA-TuM5 Physical and Chemical Characterization of Solid Pu and Np Sources after Multi-year Exposure to Environmental Conditions**, ***Brian Powell***, Clemson University **INVITED**

A field scale radionuclide vadose zone transport experiment at the United States Department of Energy Savannah River Site is being operated by Savannah River National Laboratory and Clemson University scientists. In this experiment, plutonium and neptunium solid sources are buried in 61 cm long x 10 cm diameter lysimeters which are open to precipitation. Such experiments provide the opportunity to observe changes in the microcrystalline structure of plutonium and neptunium solid phases under various environmental conditions. In the current experiments, sources of neptunium and plutonium in multiple initial oxidation states and chemical forms have been deployed for 2-5 years of field exposure. These sources include $Pu(V)NH_4CO_3(s)$, $Pu(IV)(C_2O_4)_2(s)$, $Pu(III)_2(C_2O_4)_3(s)$, $Pu(IV)O_2(s)$, $Np(IV)O_2(s)$ and $NpO_2NO_3(s)$. X-ray absorption spectroscopy (XAS) analysis of initially $Pu(V)NH_4(CO_3)$ sources archived in an inert atmosphere and sources exposed to lysimeters indicate some reduction to Pu(IV) within the sources leading to the formation of $Pu(IV)O_2(s)$. Thus, there appears to be an auto-reduction of $NH_4Pu(V)CO_3(s)$ to $Pu(IV)O_2(s)$ even under inert conditions. However, solvent extraction on archived and field-deployed sources show the archived source still contains around 40% Pu(V) whereas the same source from a field lysimeter deployed for 2.5 years contained less than 10% of Pu(V). XAS and electron microscopy studies have demonstrated differences between $Pu(IV)O_2(s)$ formed via reduction of $Pu(V)O_2NH_4CO_3$ and initially $Pu(IV)O_2$ formed from precipitation of a Pu(IV) solution. The behavior of initially $Np(IV)O_2$ sources was quite different showing oxidation to Np(V) and subsequent downward transport of more soluble $Np(V)O_2^+$. The oxidation of $Np(IV)O_2(s)$ leads to formation of a much more disordered solid phase with a significantly altered morphology than the initial $Np(IV)O_2(s)$. The results of these experiments will be discussed in terms of evaluating the history of the sample through analysis of the microcrystalline structure and the influences of aging under various environments.

11:00am **AC+AS+SA-TuM10 Synchrotron Radiation Investigation of f-element Extraction from a Carboxylic Acid Functionalized Porous Aromatic Framework**, ***David Shuh***, Lawrence Berkeley National Laboratory, *S. Demir, N.K. Brune,* University of California Berkeley, LBNL, *J.F. Van Humbeck, J.A. Mason,* University of California Berkeley, *T.V. Plakhova,* Lomonsov Moscow State University, Russia, *S. Wang,* University of California Berkeley, LBNL, *G. Tian, S.G. Minasian, T. Tysliszczak,* Lawrence Berkeley National Laboratory, *T. Yaita, T. Kobayashi,* Japan Atomic Energy Agency, *S. Kalmykov,* Lomonsov Moscow State University, Russia, *H. Shiwaku,* Japan Atomic Energy Agency, *J.R. Long,* University of California Berkeley

Porous aromatic frameworks (PAFs) incorporating a high concentration of acid functional groups possess characteristics that are promising for use in separating lanthanide and actinide metal ions, as required in the treatment of radioactive waste. These materials have been shown to be indefinitely stable to concentrated acids and bases, potentially allowing for multiple adsorption/stripping cycles. Additionally, the PAFs combine exceptional features from metal organic frameworks (MOFs) and inorganic/ activated carbons giving rise to tunable pore surfaces and maximum chemical stability. The adsorption of selected metal ions, $Sr^{2+}$, $Fe^{3+}$, $Nd^{3+}$, and $Am^{3+}$, from aqueous solutions employing a carbon-based PAF, BPP-7 (Berkeley Porous Polymer-7) has been investigated. This material displays high metal loading capacities together with excellent adsorption selectivity for neodymium over strontium. X-ray absorption spectroscopy studies show that the stronger adsorption of neodymium is attributed to multiple metal ion and binding site interactions resulting from the densely functionalized and highly interpenetrated structure of BPP-7. Recyclability and combustibility experiments demonstrate that multiple adsorption/stripping cycles can be completed with minimal degradation of the polymer adsorption capacity.

11:20am **AC+AS+SA-TuM11 The Effect of $Al_2O_3$ Encapsulation Using Atomic Layer Deposition on the Photoluminescent, Water and Thermostability Properties of $SrAl_2O_4$ Based Phosphors**, ***Erkul Karacaoglu***, *E. Özturk,* Karamanoglu Mehmetbey University, Turkey, *M. Uyaner,* Selcuk University, Turkey

Aluminate based phosphors ($MAl_2O_4$, $M_4Al_{14}O_{25}$, M= Sr, Ba, Ca, etc.) are chemically unstable against water and even moisture. Moreover, some of phosphors, like green emitting phosphorescent materials' luminescence properties, but not their structural properties, are affected negatively during reheating applications because the 2+ ionic state of europium is oxidized to 3+ in open atmosphere low temperature heating process thus limiting their applications. Their hydrolysis process were studied and analyzed intensively by researchers. Changes of pH value of suspensions, the structures and optical properties of the hydrolysis of phosphor structures had been investigated. In this research, to prevent or minimize this degradation, to enhance the water resistance and to maintain the phosphorescence properties, an $Al_2O_3$ coating on the surface of $SrAl_2O_4$ based phosphor pellets (1 mm thickness) were prepared using Atomic Layer Deposition (ALD) method with Trimethylaluminum (TMA) precursor. The investigation of phase formation of strontium aluminate was analyzed by thermal analysis (DTA/TG) until 1500 °C. The $SrAl_2O_4$ with Monoclinic structure in single phase having lattice parameters a=8.44365 Å, b=8.82245Å, c=5.15964Å and $\alpha$=90° $\beta$=90° $\gamma$=90° were obtained according to XRD analysis. The photoluminescence (PL) results of both open and reduced atmosphere synthesized phosphors with excitation and emission wavelengths and decay time were determined by a PL spectrometer at room temperature. The reduced and open atmosphere synthesized samples have different photoluminescent characteristics because of ionic state of europium in 2+ and 3+ at reduced atmosphere and open atmosphere, respectively. Moreover, it was obtained that the main crystal, $SrAl_2O_4$, had photoluminescent properties. The surface analysis of phosphors as morphology and elemental analysis (SEM/EDX), X-ray diffraction (XRD), water and heat resistance (thermostability), photoluminescence (PL) of the phosphors before and after encapsulation were discussed in detail.

## 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.

[1] E.W.B. Dias, H.S. Chakraborty, P.C. Deshmukh, S.T. Manson, Breakdown of the Independent Particle Approximation in High-Energy Photoionization, (1997) 4553–4556.

[2] W. Drube, T.M. Grehk, S. Thieß, G.B. Pradhan, H.R. Varma, P.C. Deshmukh, S.T. Manson, Pronounced effects of interchannel coupling in high-energy photoionization, 46 (2013). doi:10.1088/0953-4075/46/24/245006.

[3] A. Herrera-Gomez, M. Bravo-Sanchez, F.S. Aguirre-Tostado, M.O. Vazquez-Lepe, The slope-background for the near-peak regimen of photoemission spectra, J. Electron Spectros. Relat. Phenomena. 189 (2013) 76–80. doi:10.1016/j.elspec.2013.07.006.

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, $\sigma$ (1), corrected for transmission function, T, and escape depth, $\lambda$.

Using clean elemental surfaces the validity of using relative $\sigma$’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 $\sigma$’s, or variations in intensity losses to satellites, invalidating the use of main peak intensities plus $\sigma$ values ($\sigma$ includes intensity from all final states). $\sigma$ 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 $\sigma$’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 $\sigma$ should be used when relying on main peak intensities.

1 J. H. Scofield, J. Elec. Spec. 8, 129 (1976)

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)

3. R. P. Gupta and S. K. Sen, Phys. Rev. B , 15 (1975)

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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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## Electronic Materials and Photonics Division
## Room: 14 - Session EM+NS-TuM

## Nanostructures and Nanometer Films for Electronic and Photonic Devices

**Moderators:** Jessica Hilton, RHK Technology, Joseph Tischler, U.S. Naval Research Laboratory

8:00am **EM+NS-TuM1 Spin Properties in Semiconductor Colloidal Quantum Dots**, ***Efrat Lifshitz***, Russell Berrie Nanotechnology Institute, Solid State Institute, Israel **INVITED**

Colloidal semiconductor quantum dots (CQDs) have been at the forefront of scientific research for more than two decades, based on their electronic and optical tunable properties. Recent years show a substantial interest in spin properties with significant importance for spin-electronic, spin-photovoltaic and spin-optical devices.

The talk includes the study of two different CQD platforms: (1) CQDs from the II-VI semiconductors and their diluted magnetic derivatives; (2) Halide perovskite CQDs. Both systems show intriguing spin properties of special scientific and technological interests.

**Spins in CdSe/CdS and $Mn^{+2}$@CdSe/CdS**: Unpaired spins generated by an absorption of a phonton (electron and hole) can dictate the magneto-optical properties of the host CQDs. Furthermore, magnetic doping by foreign ions (e.g., Mn), induces internal spin interactions between photo-generated species and the dopant spins, leading to giant magnetization. The current study developed a method to position the Mn ions selectively either at the core or at the shell, by which, controlling the electron-guest versus hole-guest exchange interaction. The materials were characterized by magneto-optical methods, including optically detected magnetic resonance, uncovered individual interactions with resident carriers, thus, revealing understanding of a control of a magnetism with a benefit for spin-based devices.

**$APbBr_3$ (A=Cs$^+$, methylamonium)*:** The perovskites are minerals that have been studied extensively in the past. They are the focus of new interest in recent years, due to their exceptional performance in photovoltaic cells. Perovskites semiconductors possess high absorption coefficients as well as long-range transport properties. Currently, they are also prepared in the form of CQDs with very interesting properties including ferroelectricity, magnetism and exciton effects. The magneto-optical measurements of excitons in $APbBr_3$ as individuals were investigated by monitoring the micro-photoluminescence spectra in the presence of an external magnetic field, while monitoring either the circular or linear polarization components. Gradual band splitting occurring upon the application of a magnetic field, deviating from a common Zeeman interaction behavior, proposes the existence of a more complex mechanism, when Rashba split is one of the plausible interpretations.

*Collaboration with M. Kovalenko and A. Rappe

9:00am **EM+NS-TuM4 A Platform for Growth of Crystalline Thin-Film Compound Semiconductors on Oxides, Metals, and 2-D Materials**, ***Rehan Kapadia****, D. Sarkar, W. Wang*, University of Southern California

The electronic and photonic circuits and systems that form the backbone of the modern world are predicated on the ability to create high quality semiconductors. Yet, high-performance electronic and photonic grade semiconductors are nearly exclusively grown on lattice matched substrates. This substrate limitation arises due to the fundamental mechanisms of nucleation and growth in state-of-the-art vapor phase growth techniques, which proves to be extremely limiting and costly. Here we demonstrate a platform for growth of compound semiconductors from microscale liquid metal templates. Using these templates, we can control nucleation and growth of these compound semiconductors, enabling single crystalline devices on non-epitaxial substrates. To grow single crystalline material in the desired form-factors, from liquid metal templates on arbitrary substrates presents a significant challenge, as dewetting of the liquid films prevent control over the ultimate material geometry. Through a basic thermodynamic approach, we show that it is possible to control dewetting on nearly any material, and subsequently grow compound semiconductors on these same substrates. Using this approach, we demonstrate growth and characterization of crystalline InP, InAs, and GaP, on silicon nitride, graphene, gadolinium oxide on silicon, and metals.

Next, we show that compound semiconductors with multiple stable phases can be grown phase-pure using this approach, using tin phosphide as the example. We show that through tuning the growth conditions, we can control which stable phase of tin phosphide precipitates and grows. This control illustrates that our approach is useful for materials beyond simple III-V and II-IV compounds, which only have one stable phase. By carrying out these growths at significantly non-equilibrium conditions, we demonstrate ternary InGaP alloys, with stoichiometry control over nearly the entire In-Ga composition range. Unlike binary III-V or the Sn-P system, where the stoichiometry of the precipitating compound is nearly insensitive to the growth conditions, the ternary systems are alloys, and consequently extremely sensitive to growth conditions, making growth of uniform materials a potential challenge. We show that through control over the growth conditions, we can achieve high-quality, uniform stoichiometry ternary III-V alloys. Finally, we show that by enabling nanoscale phase segregation during growth of these ternary alloys, we can materials with extremely broadband photoluminescence curves, with FWHMs greater than 600 meV, potentially enabling a new class of broadband light sources.

9:40am **EM+NS-TuM6 Nanometer Thick Diffused Metal Oxide Light Sensing Film Structures**, ***Fred Cadieu***, Queens College of CUNY and Graduate Center of CUNY, *J.S. Monaco*, Queens College of CUNY, *L. Mourokh*, Queens College of CUNY and Graduate Center of CUNY

Approximately 10 nm thick light sensing film structures have been fabricated by sequentially sputtering various metals in oxygen, then in argon, and then in oxygen again. The layers have been deposited onto heated silicon substrates to create a diffusion region. The layered thicknesses were calibrated by x-ray reflectivity measurements. The film layers, being mostly oxides, exhibit a high lateral resistivity so that the current path is through the film thickness between a grid of contacts deposited below and on top of the film structures. For such current, a high degree of light sensitivity, and voltage polarity sensitivity, has been observed.[1] Analogous film structures have been fabricated using hafnium,[2] titanium,[2] and aluminum such that exposure to light causes large increases in currents for one voltage polarity, but little or no effect for the opposite polarity. The observed phenomenology has been shown to be consistent with a single-particle model based on the existence of interface states on the metal-oxide interfaces.[2] The details of light sensitivity and current polarity sensitivity are dependent on the deposition temperatures and thicknesses of the film layers. Hafnium based interfaces respond repeatedly to light pulses with current pulses up to several hundred microamperes, while aluminum based interfaces can only respond repeatedly with current pulses up to several tens of microamperes.

1. F.J. Cadieu, Device with Light-Responsive Layers. US Patent No. 9,040,982.

2. F.J. Cadieu and Lev Murokh, Nanometer Thick Diffused Hafnium and Titanium Oxide Light Sensing Film Structures, *World Journal of Condensed Matter Physics***7**, 36-45 (2017).

11:00am **EM+NS-TuM10 Integration of Metallic Nanoparticles in Sensing and Memory Devices for Resistance Modulation and Enhanced Switching**, ***Dimitris Tsoukalas***, National Technical University of Athens, Greece **INVITED**

In this work we present the fabrication of metallic nanoparticles (NPs) in vacuum at room temperature and their incorporation into sensor or memory two terminal devices emphasizing their influence on device resistance modulation or switching. Nanoparticles were manufactured using the gas phase condensation technique with a target of high purity. The NPs production system consists of a smaller vacuum chamber (Nanogen) which is connected via an aperture of diameter ~ 3 mm with a larger central vacuum chamber in which the sample holder is mounted. The Nanogen chamber is equipped with a DC magnetron sputtering head and in between the Nanogen chamber and the central chamber there is a pressure gradient, the pressure in the Nanogen being around $10^{-1}$ mbar while in the main chamber pressure is $10^{-4}$ mbar. The atoms produced by the magnetron sputtering because of the high pressure in the Nanogen chamber, undergo a short free path, colliding with the atoms of the inert gas (Ar) and lose part of their kinetic energy. This leads to the creation of a supersaturated vapor of the target material, which is condensed, causing the atoms to form nuclei from the material. Due to the pressure gradient prevailing, these nuclei move towards the central chamber. During this movement they interact among them to form larger NPs finally entering into the central vacuum chamber through the aperture.

Regarding the application of nanoparticle networks to sensors, our group is focusing in the use of metallic NPs in particular for chemical, bio and strain sensing applications. We first review the principle of operation of such devices that is based on the change of percolation current through the NP network when the interspace distance among NPs is modified by an external stimuli. We then discuss the potential of integrating these sensors on flexible substrates as well as the influence on their performance of a protective aluminum oxide coating deposited over the nanoparticle network.

Resistive switching memories (RRAM) based on metal oxides are emerging as a new research field and at the same time are intensively studied as one of the most promising candidates for future non-volatile memory applications. We demonstrate that a wide range of non-volatile memory properties can be affected and improved by embedding NPs into the metal oxide matrix. The concentrated electric field effect around the nanoparticles in combination with the charge trapping effect, are regarded as the driving forces for the recorded switching patterns. As a result NPs increase the on/off switching ratio and at the same time decrease the inherent variability of RRAM.

11:40am **EM+NS-TuM12 Thin-film Metallic Glass: An Effective Diffusion Barrier for Microelectronic Packaging, CIGS Solar Cell and Thermoelectric Modules**, *C.C. Yu*, National Taiwan University of Science and Technology, Taiwan, Republic of China, *H.J. Wu*, National Sun Yat-sen University, Taiwan, Republic of China, ***Jinn Chu***, National Taiwan University of Science and Technology, Taiwan, Republic of China

Thin film metallic glass (TFMG) with its amorphous nature is of great interest owing to its unique properties, including high strength, large elastic limits, excellent corrosion and wear resistance. For many electronics, the atomic inter-diffusion may cause device failure or performance degradation during either fabrication or operation. Thus, the introduction of diffusion barrier layer in the device is a common approach to solve this problem. Crystalline Ni- or Ti-based layers are the most common materials for diffusion barriers. Nevertheless, grain boundaries are generally considered as atomic diffusion path, and thus crystalline metals are not able to block diffusion effectively. TFMG, possessing grain boundary-free structure, is thus thought to efficiently mitigate atomic diffusion.

In this presentation, we report the effects of thin film metallic glass as diffusion barriers on the Sn whisker mitigation in the Cu-Sn couples and the copper indium gallium selenide (CIGS) solar cells on stainless steel (SS) as well as the mid-temperature thermoelectric module. We found that TFMG effectively blocks the Cu/Sn interaction even with the thickness as thin as 25 nm. In addition, with very thin thickness, the introduction of TFMG layer is expected to yield insignificant degrees of compressive stress, which is anticipated to occur when the samples are exposed to thermal cycling. Furthermore, the detrimental iron diffusion from SS into CIGS is found to be effectively hindered by the introduction of a 70-nm-thick TFMG barrier; the cell efficiency is thus from 2.73 for bare sample to 5.25% for the one with

TFMG barrier. For application in thermoelectric module, a 200 nm-thick Zr-based TFMG, acting as an effective diffusion barrier layer with low electrical contact resistivity, was deposited on a high-zT Se-doped AgSbTe$_2$ substrate. The reaction couples structured with TFMG/TE were annealed at 673 K for 8–360 hours and analyzed by electron microscopy. No observable intermetallic compounds were formed at the TFMG/TE interface, suggesting the effective inhibition of atomic diffusion.

12:00pm **EM+NS-TuM13 Ultra-Fast Silicon Photodiodes Achieve High Efficiency via the Integration of Light-trapping Micro-/nanoholes**, ***Hilal Cansizoglu***, *Y. Gao, K.G. Polat, S. Ghandiparsi, C. Bartolo Perez, A. Kaya, H.H. Mamtaz, A.S. Mayet,* University of California, Davis, *E. Ponizovskaya Devine*, W&WSens Devices, Inc., *Y. Yamada*, University of California, Santa Cruz, *A.F. Elrefaie, S.Y. Wang*, W&WSens Devices, Inc., *M.S. Islam*, University of California, Davis

Surface-illuminated photodiodes (PDs) for ultra-fast data transmission are typically GaAs-based non-CMOS compatible detectors. Silicon (Si) has long been ignored for being a material of choice in ultra-fast communication links due to its poor responsivity for the wavelengths >800 nm at data rates 10 Gb/s or higher. Recent demonstration of CMOS compatible surface-illuminated Si PDs with photon-trapping micro-/nanoholes paves the way for the use of Si at 25 Gb/s or higher data transmission rate. Such PDs provided ≤30 ps full-width at half-maximum (FWHM) and above 50% quantum efficiency (QE) at 850nm, which is over 400% higher than the QE that a similar Si PD without absorption-enhancement micro-/nanoholes can provide. The micro/nanoholes create an ensemble of modes that radiate laterally by photon trapping and slow light effects, resulting in absorption enhancement in a very thin layer of Si (<2µm) which is required for high speed operations. The broadband efficiency enhancement by photon-trapping micro-/nanoholes enable Si to be considered as the PD material at longer wavelengths (>870 nm) which is below the room temperature bandgap of GaAs. Such broadband and enhanced efficiency of Si integrated with micro-/nanoholes can be useful for applications such as short wavelength division multiplexing (SWDM, 850-980 nm) for data centers, automotive laser radar systems (LIDAR, 850 or 905 nm) and high-performance computers (990-1065 nm). The CMOS-compatible fabrication of micro-/nanoholes can allow Si PDs to be monolithically integrated with CMOS/BiCMOS integrated circuits such as transimpedance amplifiers, equalizers, limiting amplifiers and other application specific integrated circuits (ASIC), which can increase the achievable data rate to more than 50 Gb/s.

## Exhibitor Technology Spotlight Workshops
## Room: West Hall - Session EW-TuM

### Exhibitor Technology Spotlight
**Moderator:** Chris Moffitt, Kratos Analytical, Inc.

10:20am **EW-TuM8 Development of a Novel Single Cold Cathode Ionization Gauge with Operation from High Vacuum to Atmosphere using Advanced Manufacturing Techniques**, ***Dave Kelly***, *G. Brucker*, MKS Instruments, Inc., Pressure and Vacuum Measurement Group

Cold cathode ionization gauges (CCIGs) have been used for decades to make high vacuum measurements on a variety of production equipment. Traditionally, wide-range CCIGs involve multiple gauge techniques for pressure measurement, making this technology cost-prohibitive and not as robust for many industrial applications. In order to expand the scope of CCIG technology to address cost-sensitive and rugged applications, we have developed an innovative wide-range CCIG. This new CCIG utilizes a one gauge technique – gaseous discharge – which is capable of measuring pressures from high vacuum to atmosphere. Advanced manufacturing techniques were employed that allowed for the testing and selection of low-cost construction materials that are well suited for industrial environments. Moreover, these manufacturing techniques allowed for a design of this new gauge to be easily serviceable during routine preventive maintenance cycles, lowering the overall cost of ownership for a given application. The result of this development yielded a manufacturable low-cost wide-range CCIG capable of accuracy that meets the needs of the industry from 1E-7 Torr to atmosphere.

10:40am **EW-TuM9 New Developments from Thermo Fisher Scientific**, ***Timothy Nunney***, *P. Mack, C. Deeks, A. Bushell*, Thermo Fisher Scientific, UK

In this presentation we will highlight the latest developments in surface analysis and materials analysis instrumentation from Thermo Fisher Scientific.

## 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.

[1] S. Pollard et al. "Observation of stable Néel skyrmions in cobalt/palladium multilayers with Lorentz transmission electron microscopy" Nat. Comm. 8, 14761 (2017).

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 $\mu_B$, 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.

References:

[1] M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, and J. M. D. Coey, Phys. Rev. Lett. 93, 177296 (2007)

[2] E. F. Arguelles, S. Amino, S. Aspera, H. Nakanishi, and H. Kasai, J. Phys. Soc. Jpn. 84, 045002 (2015)

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.

## MEMS and NEMS Group

## Room: 24 - Session MN+BI+EM+SS+TR-TuM

### Microelectromechanics: Relays to RF/Surfaces in Micro- and Nano- Systems

**Moderators:** Sushma Kotru, The University of Alabama, Roya Maboudian, University of California at Berkeley

8:00am **MN+BI+EM+SS+TR-TuM1 The Industrialization of MEMS through Materials Innovations**, ***Chris Keimel***, Menlo Micro **INVITED**

For the past 150 years, the mechanical relay was one of the original building blocks of electrical systems, for power electronics, controls, and even computing. With the introduction of the transistor in the middle of the 20th century, many industries were transformed with the introduction of ubiquitous, low-cost switches (solid-state) that could be manufactured by the billions with highly advanced equipment and manufacturing processes. Still today, many industries, especially power distribution and controls, are still not able to live with the tradeoffs of solid-state technologies (leakages, losses, lack of air-gap, thermal) and continue to employ large, slow, and costly mechanical relays which have evolved only slightly over the past 50+ years. The miniaturization of the mechanical relay through MEMS technology, coupled with materials innovations, will enable a new class of devices capable of connecting (wireless control) and controlling (distributed power) today's and the futures billions of automated electrical nodes.

We have developed electrostatically actuated MEMS relays capable of switching in ~3usec, sustaining more than 400V across its open contacts and controlling loads of 10s of watts to a few kilowatts. Ohmic MEMS switch with creep resistant metal alloy beams, and a highly reliable ruthenium contact has been developed based on methodical failure mode analysis taking into account material, mechanical and electrical constraints. The ohmic relays, when applied to RF applications, deliver multi throw configurations capable of <0.3dB insertion loss from DC to 3GHz combined with the ability to handle 25W of RF power.

A metal MEMS switch technology has been developed from the ground up through material, process, device, package and electronic integration innovations. The combination of fast microsecond switching speed and broadband (DC to RF) signal operation along with the ability to control amperes of current and sustain hundreds of volts across micron sized air gaps has enabled the miniaturization of the mechanical relay for broad ranging applications from wireless infrastructure to the Industrial IOT.

8:40am **MN+BI+EM+SS+TR-TuM3 Electron-Phonon Waltz: Acoustoelectrics in MEMS**, ***Dana Weinstein***, Purdue University **INVITED**

The Acoustoelectric (AE) effect is a result of the interaction between free charge carriers and the electrical deformation potential produced by a propagating elastic wave in the piezoelectric. When an external DC electric field is applied across the semiconductor in the direction of the propagating wave, a drift velocity ($\nu_d$) is imparted to the free carriers. If the drift velocity is slower than (or opposite to) the acoustic wave velocity ($\nu_s$), the electrical deformation potential lags behind the strain wave. This phase lag not only decreases the acoustic wave velocity, but also transfers energy from the acoustic wave to the electrons, increasing the acoustic losses. When a sufficient DC field is applied to cause the drift velocity to exceed the acoustic wave velocity, the electrical deformation potential now leads the strain wave. This transfers energy from the electrons to the acoustic wave, resulting in an increased acoustic velocity and net acoustic gain [1,2,3,4].

A large body of work based on AE was established in the 1960s and 70s, resulting in a range of devices from phase shifters to correlators. With the development of new materials and new processing needs, there has been a recent resurgence of interest in this field, particularly for its amplifying and inherently non-reciprocal properties. Here, we discuss the implications of the AE effect for GHz frequency electromechanical signal processing. RF applications, linearity, and noise of the AE effect will be examined. Finally, benefits and limitations of prospective semiconductor/piezoelectric material systems will be discussed.

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[2] D. L. White, “Amplification of Ultrasonic Waves in Piezoelectric Semiconductors," Journal of Applied Physics, vol. 33, no. 8, pp. 2547-2554, Aug. 1962.

[3] B. K. Ridley, “Space charge waves and the piezo-electric interaction in 2D semiconducting structures," Semiconductor Science and Technology, vol. 3, no. 6, p. 542, 1988.

[4] G. S. Kino and T. M. Reeder, “A normal mode theory for the Rayleigh wave amplifier,” in IEEE Transactions on Electronic Devices, vol. 18, no. 10, pp. 909-920, Oct. 1971.

9:20am **MN+BI+EM+SS+TR-TuM5 Autonomous Oscillations of a MEMS Resonator**, ***David Czaplewski***, Center for Nanoscale Materials, Argonne National Laboratory, *C. Chen, D. Lopez,* Argonne National Laboratory, *D.H. Zanette*, Centro Atomico Bariloche and Instituto Balseiro, *S.W. Shaw*, Florida Institute of Technology

Resonant MEMS and NEMS structures are used in a wide variety of applications including mass and force sensing, time keeping, and quantum information. For all MEMS and NEMS resonators, energy is lost every cycle of oscillation to the environment (modeled as a coupled bath). If this energy is not restored by an external source, the amplitude of the resonant motion will decrease toward zero. This well-known effect is commonly referred to as “ring-down”. For linear resonators, the frequency of the resonator will remain constant and the amplitude will decreases exponentially while for non-linear resonators, the amplitude will decrease exponentially and the frequency will simultaneously decrease toward the linear response due to the amplitude-frequency (a-f) effect. However, we demonstrate a non-linear resonator that has constant frequency and an amplitude that does not decay for a given period of time (~ 0.1 s) after discontinuing the restoring energy to the system. We call this time “coherence time” because the amplitude and frequency of the oscillation does not decay when the restoring energy is removed. In essence, the resonator is autonomous during coherence time. Unfortunately or fortunately, this behavior does not violate the second law of thermodynamics. The behavior can be explained by looking at the entire system. We drive a non-linear MEMS resonator to a frequency where the primary mode couples with another internal mode. When the resonator is actively driven, the higher order mode receives energy from the primary mode. When the external energy is discontinued, this energy is restored back to the primary mode allowing the primary mode to continue to oscillate. However, once the energy stored in the higher order mode is depleted (its amplitude is near zero), the behavior of the primary mode begins to “ring-down”. During this talk, I will show characteristics of the coupled modes including operation with constant frequency and a non-decaying amplitude for a period of time with no drive.

9:40am **MN+BI+EM+SS+TR-TuM6 Metallic Glass for MEMS Microphone Device**, ***MaiPhuong Nguyen***, WPI-Advanced Institute for Materials Research (WPI-AIMR)/ Micro System Integration Center (µSIC), Tohoku University, Japan, *J. Froemel,* WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Japan, *S. Tanaka*, Graduate School of Engineering/ Micro System Integration Center (µSIC), Tohoku University, Japan

Micro Electro-Mechanical Systems (MEMS) microphones have been extensively developed and introduce into mobile phones market with high performance such as high signal to noise ratio, good sensitivity, and power consumption and good reliability in term of packages. Up to now, most studies have been focused on the improvement of sensitivity of microphone which is proportional to the compliance of the membrane. However, no significant progress has been achieved due to the limitation of material itself. Generally, single crystal and polycrystalline silicon based devices are brittle and fracture causing the interior defects during the fabrication processes. Therefore, the research of new materials to substitute polycrystalline silicon is necessary. Amorphous metals exhibit no grain boundaries, crystal defects and excellent mechanical properties such as fatigue free, large elastic limit, high strength, corrosion resistance which has been promising materials for MEMS devices such as micro-scanner, RF MEMS varactor, capacitive switch ... Metallic glasses are a kind of amorphous alloy exhibiting viscous flow at a certain temperature range so-called “supercooled liquid region”. In the supercooled liquid region, metallic glasses can be easily produced through a variety of fast-cooling methods and have excellent mechanical formability. In addition, metallic glass thin films are easily prepared on Si or $SiO_2$ substrates by sputtering technique which is compatible with MEMS processes such as photolithography, dry or wet etching and lift off processing. Therefore, characterization and fabrication of metallic glasses films deposited by sputtering for MEMS microphone will be studied.

The CoTaB films with thicknesses in the range of 100 nm to several micrometers have been successful deposited on thermal SiO2 substrates by rf-sputter technique. The amorphous structure with smooth surface and negligible magnetic property was confirmed by TEM, AFM, XRD and SQUIDS measurement, respectively. The metallic glass behavior was investigated by DSC analysis which shows the glass transition and crystalline temperature of 700 and 720.9 C, respectively. In addition, the mechanical properties such as stress, stress gradient and Young modulus have been studied by using pointer and cantilever structure. Co-based metallic glass exhibited tensile and compressive stress depending on sputter conditions, thicknesses as well as further treatment process. Additional results will be presented in detail at the conference with an emphasis on the dependence of the process conditions.

11:00am **MN+BI+EM+SS+TR-TuM10 Role of Surfaces in Assembly of Ceria Nanostructures**, ***Sudipta Seal***, University of Central Florida **INVITED**

Cerium is a rare earth element of the lanthanide series with a fluorite lattice structure. The cerium atom can exist in either 3+ or 4+ states, and may alternate between the two in a redox reaction that is more pronounced in nanoparticles. However, the physicochemical properties of a nanocrystal assembly can be different from the properties of both the individual nanoparticles and the bulk phase. We have synthesized ceria nanoparticles in various medium and studied the self-assembly of particles to octahedral and star shaped nanostructure assembly. It was further identified that the concentration of Ce4+ in nanoceria decreases over time, further controlling the surface chemistry. We will also highlight some of the key aspects of self-assembly of $CeO_2$ into nanorods. The surface area available and the orientation of crystallographic planes in ceria nanostructures highly regulate the catalytic property at nanoscale as evident by high resolution TEM. Further we discuss the role of Madelung energy and its relation to the catalytic activity, which is important in sensing and other analyte interactions. The surface chemistry or the ratio of $Ce^{3+}/Ce^{4+}$ can be extensively modulated by the assembly process. At the end we report, the feasibility of a novel $H_2O_2$ based electrochemical sensor that directly measures the current response of multivalent ceria in presence of $H_2O_2$. The fabricated sensor showed a picomolar range limit of detection while remaining insensitive to interfering species. Peroxide sensing is very important in biologically relevant oxidative stress in cells. It was observed that a lower ratio of $Ce^{3+}:Ce^{4+}$ redox states elicits a greater current response towards $H_2O_2$ The detection of such electroactive analytes make it easier to detect using normal nanoparticle modified electrodes, thereby eliminating the use of organic mediators.

11:40am **MN+BI+EM+SS+TR-TuM12 Optimization and Nano-characterization of Electrostrictive Response of Gd-doped Ceria Actuators**, ***Sidney Cohen***, *E. Mishuk, E. Makagon, E. Wachtel, K. Rechav, R. Popovitz-Biro, I. Lubomirsky*, Weizmann Institute of Science, Israel

Gd-doped ceria (GDC) recently attracted great interest due to its non-classical (non-Newnham) electrostrictive behavior. Although the material is well-known for its ionic conduction properties and use in solid-oxide fuel-cells, it also holds great promise for incorporation into MEMS devices because it is completely inert with respect to silicon compounds. The fact that GDC is lead-free is particularly appealing.

Here, we demonstrate fabrication and testing of membrane actuators formed with near 100% yield by a relatively simple, low temperature process. Preparation of these devices involves magnetron-sputtering of a thin film of GDC onto Si, and further processing using standard micromachining, resulting in free-standing membranes. Bridge and cantilever structures have been fabricated as well, to explore the possibility for diverse functional devices. The films were structurally characterized by electron microscopy and by x-ray diffraction, whereas electrical characterization was performed using impedance spectroscopy and cyclic voltammetry. These electrical tests revealed details of the conduction mechanism, role of the contacts, and charge-trapping.

Scanning probe microscopy was applied to quantitatively characterize the energetics and mechanics of the electromechanical response: Displacement of a circular membrane was measured by recording displacement of the cantilever probe under feedback as a function of frequency and applied voltage, and temporal Joule heating recorded using a scanning thermal probe. These measurements support calculations of heat-induced strain at high frequencies. These measurements showed that displacements obtained are sufficient for practical applications and provided insights on the factors controlling performance.

12:00pm **MN+BI+EM+SS+TR-TuM13 Sustainable Thermoregeneration of Plastrons on Superhydrophobic Surfaces**, ***Tomer Simovich***, Ruhr-University Bochum, Germany, *J. Arnott*, The University of Melbourne, Australia, *A. Rosenhahn*, Ruhr-University Bochum, Germany, *R.N. Lamb*, Canadian Light Source, Canada

A popular and desirable function of superhydrophobic coatings is their remarkable ability to retain an entrapped layer of air, called a plastron, when submerged underwater. The drawback is that the air layer is short lived due to solvation into the surrounding liquid. Liquid gas extraction has been explored for the purpose of respiration through oxygen filtering or generation via chemical reaction. Manipulating solubility through temperature has been attempted but due to its inefficiencies has not been developed further into functioning technologies. This paper introduces a novel method of extracting gas from water to generate enough air to permanently stabilize a plastron on superhydrophobic surfaces for sustained anti-fouling, rust resistance and drag reduction abilities. This method involves locally heating the liquid surrounding a superhydrophobic coating, reducing gas solubility causing the gas to migrate to the liquid-air interface. Due to the low surface energy of superhydrophobic coatings, nucleation of supersaturated gasses occurs preferentially at the coating interface, thereby replenishing the plastron. This requires a relatively low energy input, due to the small volume of water required to be locally heated combined with the small temperature differential induced between substrate and liquid. This process may be more environmentally sustainable in comparison to competing methods. With a constant supply of equilibrated water and minimal energy input, the plastron can survive indefinitely without need for the mechanical application of additional gas.

## 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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## Plasma Processing for Biomedical Applications Focus Topic
## Room: 12 - Session PB+BI+PS-TuM

## Plasma Medicine
**Moderator:** Katharina Stapelmann, Ruhr-University Bochum, Germany

8:00am **PB+BI+PS-TuM1 Spatial Distribution of Biological Effects Induced by Plasma Reactive Species**, ***Sylwia Ptasinska***, University of Notre Dame **INVITED**

Several *in vitro* and *in vivo* studies have been conducted in a variety of cancer cell lines that demonstrate the efficacy of cold plasmas in causing cell death since the advent of this new research area in the plasma physics community in 2010. Due to the complexity of both the plasma and biological systems, many questions must be answered to sharply improve our understanding of the physical, chemical, and biological processes underlying their interactions. However, since cold plasmas produce a cocktail of reactive oxygen species (ROS) and reactive nitrogen species (RNS), these species are believed to be key agents that can induce a number of biological effects, including impairment of cell substructures and even cell death. Moreover, cancer cells have proven to be more susceptible to damage by these reactive species than normal cells subjected to plasma exposure. The outcome of cell responses to plasma treatment has inspired the potential application of plasma as an effective and safe tool for novel cancer therapy. Our research focuses on investigations of nucleus DNA damage in cancer cells and bacterial inactivation caused by exposure to plasma reactive species. Initially, to detect ROS and RNS that reached the targeted biological systems we used semi-quantitative test strips, while to investigate biological effects in cells we used digital imaging or immunofluorescence microscopy. Recently, to obtain the high-resolved spatial distribution of DNA strand breaks we developed a workflow with algorithms for image analysis using CellProfiler and MATLAB, including background correction, cell segmentation, feature extraction, cell classification, and data visualization. This method well preserves the essential spatial information about cell distribution, which is critical because of the localized nature of the plasma jet treatment. By applying both supervised and unsupervised machine learning techniques to the images, we were also able to classify the cells according to different cell cycle phases, and thus obtain spatial information regarding plasma jet effects on cell cycle progression.

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*** NSTD Student Award Finalist**

8:40am **PB+BI+PS-TuM3 Mechanisms of Cell Death in Prostate Epithelial Cells after Treatment with Low Temperature Plasma**, *J. Packer, A.M. Hirst, F.M. Frame,* ***Deborah O'Connell****, N.J. Maitland*, University of York, UK

Low-temperature plasma (LTP) treatment of cancer cells have been explored for a variety of malignancies. These plasmas, operated at atmospheric pressure and close to room temperature, are efficient sources of reactive oxygen and nitrogen species (RONS), electric fields and photons, and can induce a variety of biological responses. There is an increasing clinical move towards focal therapy for more conservative management of prostate cancer, with reduced levels of common side effects such as incontinence and impotence compared with radical treatments, and promising outcomes. Low-temperature plasmas may offer such potential.

A dielectric barrier discharge jet, created within a glass tube surrounded by two electrodes (~ 6 kV applied sinusoidal voltage), with a helium plus 0.3% oxygen gas flow is used for these investigations. We have employed both purified tumour cells freshly extracted from prostate cancer patients, and matching, non-tumour cells from a distant region of the same prostate. Freshly isolated primary tumour cells acts as a near patient model, which has recently confirmed differences in pharmacological susceptibility as compared with 30 year old established cell lines.

Treatment of primary prostate epithelial cells with LTP resulted in sigificant cell death in both normal and cancer cells; and no significant selectivity observed, as commonly reported. In addition, most cells appeared to die via a necrotic mechanism, rather than apoptosis, maybe as a result of the mitochondrial toxicities of the LTP-activated reactive oxygen species (ROS). However, some autophagy was also detected, which has been shown to act as a salvage pathway for sub-lethally damaged cells.

To determine which of the multiple plasma activated bio-reactive species are responsible for the cytotoxicity, we have explored immediate and longer-term effects on gene expression, with a particular focus on oxidative responses, in multiple patient samples. Comparative studies in the established cell lines indicated a delayed and different response, highlighting that cell lines don't always reflect the response of primary cells. Expression of 84 genes (mRNA by RT$^2$ arrays from Qiagen) was assessed at multiple time points, after a 3 minute LTP treatment, and candidate genes/response pathways were identified. Immunofluorescence and western blotting were used to verify changes in protein expression. The response varied according to the clinical grade of the tumour (including a remarkable downregulation of 18 factors only seen in the highest grade tumours). All epithelial cells showed a stimulation of transcription factor-driven anti-oxidative response, as a potential resistance mechanism.

9:00am **PB+BI+PS-TuM4 Selective Antitumor Effect of the Plasma-Activated Medium Produced by Atmospheric Pressure Plasma with High Plasma Density**, ***Yohei Takahashi****, Y. Taki,* Nikon Corporation, Japan, *K. Takeda,* Meijo University, Japan, *H. Hashizume, H. Tanaka, M. Hori*, Nagoya University, Japan

Recently, atmospheric pressure plasma has been widely developed for the applications on various fields, such as synthesis approaches, surface modification, sterilization, etc. Especially, cancer therapy using atmospheric pressure plasma is one of the most attractive applications. The culture medium irradiated with the atmospheric pressure plasma was called Plasma-Activated Medium (PAM), which exhibited the selective apoptotic cell death of cancer cells. In this study, we have demonstrated the antitumor effect of medium induced by irradiation of atmospheric pressure plasma with high plasma density and compared the cell survival between cancer and normal cells, which showed that the selective apoptotic cell death was achieved. Additionally, the basic diagnostics of the plasma and the analysis of the PAM were performed and the relation with the antitumor effects was discussed. The emission peak of OH radical ($A^2\Sigma$-$X^2\Pi$) was observed in the atmospheric pressure plasma. This transition is the intense systems emitted by low temperature plasmas containing even a small amount of $H_2O$. The selective apoptotic cell death effect by treatment with PAM produced by atmospheric pressure plasma irradiation was confirmed. The survival of cancer cell after incubation in PAM was greatly lower than that of normal cell was. The productions of $H_2O_2$ and $NO_2^-$ by irradiation of high density plasma were detected by the colorimetric assay. The synergistic effect of $H_2O_2$ and $NO_2^-$ in PAM is considered to affect the proliferation of cancer cells.

9:20am **PB+BI+PS-TuM5 Multiplex Coherent Anti-Stokes Raman Scattering (CARS) Observations of HeLa Cells Cultured in Non-equilibrium Atmospheric Pressure-Plasma-Activated Medium (PAM)**, ***Kenji Ishikawa****, R. Furuta,* Nagoya University, Japan, *K. Takeda, T. Ohta, M. Ito,* Meijo University, Japan, *H. Hashizume, H. Tanaka, H. Kondo, M. Sekine, M. Hori*, Nagoya University, Japan

Non-equilibrium atmospheric-pressure plasma (NEAPP) affects cancer cells not only directly[1] but also indirectly through exposure of cells to medium irradiated beforehand with NEAPP (i.e., plasma-activated medium [PAM]).[2] Recent studies have revealed that NEAPP irradiation generates reactive oxygen and nitrogen species (RONS) in the gas phase and relatively long-lived RONS such as hydrogen peroxide, nitrites and nitrates in the aqueous phase.[3] To further elucidate a cell-death mechanism in more detail, the present study focused on the direct analysis of PAM-induced intracellular molecules such as lipids, acylglycerol, triglyceride, adiposome in HeLa cells as cervical cancer cells. Lipid droplets (LDs) are dynamic organelles with complex and interesting biological functions that go beyond mere energy storage and are important in lipid homeostasis and metabolism. To evaluate LDs, coherent anti-Stokes Raman scattering (CARS) microscopy was used. The observation-results by multiplex coherent anti-Stokes Raman scattering (CARS) microscopy elucidated the mechanism underlying the apoptosis of HeLa cells in cultivating in PAM, leading to be simultaneously occurred the exhaustion of LDs in the cells in contrast to the accumulation, while the activation of caspase-3/7 was induced, though accumulation in lipid droplets (LDs) and lipid metabolism in the normal apoptosis of HeLa cells with activation of caspase-3/7 was previously reported.

Acknowledgement: This study was supported in part by the JSPS-KAKENHI (No. 24108002).

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9:40am **PB+BI+PS-TuM6 Plasma Medicine - From Bench to Bedside**, ***Kai Masur****, T. von Woedtke, K.D. Weltmann*, Leibniz Institute for Plasma Research and Technology, Germany

During the last decade it became possible to stimulate eukaryotic cells by applying non-thermal plasma. The same plasmas can be used to kill micororgansisms - both in vitro and in vivo. However, there is the need to understand the processes of how electrical fields, ROS /RNS and UV generation influence the cellular activities in order to find the balance between stimulating or killing biological matter. Therefore, much effort had been done by in order to control the plasma components and finally modulate biological activities. It was shown before that argon plasma treatment leads in a time dependent manner to an activation of cell proliferation in human skin samples. Furthermore, it is known that non-thermal plasma is able to diminish bacterial load of cultured microorganisms *in vitro* independent of the strain. Even more, plasma reduces the amount of antibiotic resistant bacteria in the same manner as their non-resistant strains.

In 2013, new developed plasma sources were certified as medical products and since than those devises are in clinical application. Here we report on our findings on plasma treated chronic wounds and the efficacy of non-thermal plasma. There is a very promising rate of healed and improved wounds, which demonstrate that plasma indeed can help patients with chronic wounds. However, there are some discrepancies between *in vitro* findings and results from patient treatment. The bacterial reduction is lower than in *in vitro* studies, but skin regeneration seems not to be dependent on complete bacterial removal. On the other hand, patient treatment reveals new facts about the positive effects of plasma treatment of persisting wounds. Here we summarize the positive results of plasma mediated stimulation of patients with chronic wounds.

11:00am **PB+BI+PS-TuM10 Plasma Medicine, RONS, Tissue and Cell Models**, ***Rob Short***, University of Lancaster, UK, *E. Szili*, University of South Australia, Australia **INVITED**

Electrically-generated cold plasma gas discharges are being intensively researched for novel applications in medicine and biology. Significant attention is being given to the reactive oxygen and nitrogen species (RONS), initially generated upon plasma-air interactions that are delivered to biological systems. The effects of plasma exposure are observed deep within tissue, to millimetre depths and within cells. However, very little is known about the exact nature of the initial plasma-tissue interactions, including RONS speciation and delivery depth, or how plasma RONS intervene in biological processes. In this presentation I will focus on current research using tissue and cell models to learn more about the plasma delivery and transport of RONS into tissue and cells. I will argue this research is vital to establishing an underpinning knowledge that is needed to realise the full potential of plasma in medicine and biology.

11:40am **PB+BI+PS-TuM12 Non-thermal Plasmas in Biomedical Applications– Beyond the Long Lived Species**, ***Kristian Wende****, J. Volzke,* INP Greifswald, Germany, *J-W. Lackmann*, Ruhr University Bochum, Germany, *H. Jablonowski, S. Bekeschus,* INP Greifswald, Germany, *K. Stapelmann*, Ruhr-University Bochum, Germany, *S. Hasse,* INP Greifswald, Germany, *P.J. Bruggeman*, University of Minnesota, *K.D. Weltmann*, INP Greifswald, Germany

Non-thermal plasmas have reached evidence level 2 regarding acceleration of wound healing and in certain aspects of cancer treatment, with a growing community of physicians successfully using it (plasma medicine). Key players in such biomedical applications are reactive oxygen or nitrogen species (ROS/RNS), which are deposited in either tissue (in vivo) or liquid (in vitro) and subsequently influence cellular redox signaling. A huge variety of plasma sources for potential application has been developed and comparing these sources in respect of safety and efficacy remains challenging but desirable.

One aspect can be the identification and quantification of the sources ROS/RNS deposition in liquids. However, due to the short lifetime of many ROS/RNS and limited specificity of available probes their detection is demanding. To meet this challenge, we applied a variety of analytical techniques including high-resolution mass spectrometry of small molecules (cysteine, tyrosine), ion chromatography (RNS detection), electron paramagnetic resonance spectroscopy (O, $O_3$, $^1O_2$, $O_2^-$, OH), and colorimetric assays to infer on dominant active species. Two argon plasma jets (MHz jet kinpen, RF jet) and a helium based RF jet (COST jet) were investigated. In addition, cell biology experiments allowed a first estimation of the biological impact of plasma treated small molecules.

A large number of covalent modifications have been detected and in part identified. The majority of changes to the chemical structure of cysteine was found in the vicinity of the thiol group, while in tyrosine the aromatic ring was targeted. The resulting products also occur in physiological situations in vivo, allowing to conclude that the covalent modification of small organic molecules is part of the mechanism of direct plasma-cell interaction. Predominantly short-lived oxygen species were found to be of relevance regarding the chemical and biological impact of plasma, challenging the popular concept of remote treatment (e.g. plasma treated buffers).

12:00pm **PB+BI+PS-TuM13 Effects of Oxygen or Water in Plasma Jet Environment and Feed Gas on DNA Damage**, ***Ek Adhikari***, *V. Samara, S. Ptasinska*, University of Notre Dame

Atmospheric pressure plasma jet (APPJ) sources have been explored for applications in industry and medicine. Since environmental conditions such as room temperature and humidity fluctuate, two identical APPJ sources operating at various places and time might perform differently. An APPJ operating in a controlled environment may be able to overcome that issue. Moreover, the interaction of plasma components (e.g., ions, electrons, UV light) with the air in the atmosphere generates the reactive oxygen species (ROS) and reactive nitrogen species (RNS) in the plasma jet [1]. These reactive species can be controlled by adjusting a fraction of oxygen and water vapor in the plasma jet environment and the feed gas. To create a controlled environment for a plasma source, a helium APPJ source was operated in a cylindrical glass chamber with an ambient pressure and filled with pure nitrogen gas along with a fraction of oxygen and water vapor. This APPJ source was used to induce damage in aqueous DNA. The fraction of different types of damaged DNA such as single strand breaks (SSBs) and double strand breaks (DSBs), which were induced due to plasma irradiation, and undamaged DNA were quantified by using agarose gel electrophoresis. We observed that a moderate amount of oxygen and water vapor in the environment, as well as in the feed gas, increases the level of DNA damage.

1. K. Arjunan, V. Sharma, and S. Ptasinska, Int. J. Mol. Sci. **16**, 2971 (2015).

## Plasma Science and Technology Division
## Room: 23 - Session PS-TuM

## Advanced FEOL/Gate Etching

**Moderators:** Kazunori Koga, Kyushu University, Japan, Erwine Pargon, CNRS-LTM, Université Grenoble Alpes, France

8:00am **PS-TuM1 Highly Selective Silicon Dry Chemical Etch Technique for 7nm FinFET Technology and Beyond**, *Z. Bi*, ***Thamarai Devarajan***, *L. Young, B. Miao, S. Devries, N. Loubet, C. Yeung, J. Zhang, A. Greene, H. Zhou, M. Wang, J. Strane,* IBM Semiconductor Technology Research, *Y. Yao,* IBM, *D. Canaperi, C. Surisetty*, IBM Semiconductor Technology Research

With transistor scaling in 7nm technology and beyond, fin spike removal and dummy gate silicon pull are considered to be among the most challenging hurdles in FinFET process development. In this paper, we present a plasma free dry chemical etch technique utilizing $NF_3$ and $H_2$ for selective etching of single crystal and polycrystalline silicon at various FinFET device process steps. It was demonstrated that this technique could completely remove poly silicon in vertically high aspect ratio (AR>5) nanosheet FinFET gates with larger process window (overetch budget ~200%), lower gate leakage current and much higher device yield, compared to the technique used in previous generations. Proper surface preparation, queue time control, and etch byproduct removal strategies are discussed. The residue-free etch and etch by-product sublimation mechanisms are also investigated by High Resolution Electron Microscopy (HREM) and Fourier Transform Infrared Spectroscopy (FTIR) surface analysis.

8:20am **PS-TuM2 Anisotropic and Selective Isotropic Etching of Si / SiGe Multilayers in Surface Wave Plasmas**, ***Nick Joy***, *S.A. Voronin, P. Biolsi*, TEL Technology Center, America, LLC, *A. Ranjan*, Tokyo Electron Miyagi Limited, Japan

As the feature size of planar devices reaches some fundamental limitations, the continuing drive to increase device density has led to new 3D designs such as fin FETs, nanowire, and vertical FET designs. These innovations bring their own set of challenges for etch applications. While planar devices relied more on anisotropic etching, 3D devices require more isotropic etch capabilities with high selectivity between different materials. For example, one strategy to form nanowire channels is to use multilayered Si/SiGe films that are etched vertically with an anisotropic method to define the width of the wire, and then etched laterally with a selective process that leaves isolated nanowires and allows for deposition of wrap-around gates. Such processes may require either Si selective or SiGe selective isotropic etch capabilities. These abilities have been demonstrated with a RLSA$^{TM}$ plasma etch chamber. Having spatially separated plasma generation and plasma processing regions, RLSA$^{TM}$ etchers benefit from a very low electron temperature (Te~1eV) and low self-bias voltage (i.e. low ion energy) radical-rich discharge. These conditions allow both isotropic and anisotropic selective etching of different materials.

Whether the process is selective to SiGe or Si depends on the chemistry. Generally, it is easier to etch SiGe selective to Si using fluorocarbon plasmas. The dependency of SiGe recess profiles on pressure, power, and non-fluorinated gas addition show trends that are essentially non-selective to highly SiGe (30% Ge) selective using CF4 based processes. Si selective processes are more difficult to achieve and are sensitive to specific process parameters. However, it is possible to reverse selectivity from Si:SiGe < 1 to Si:SiGe > 1 using SF6 based processes. While the etch mechanism is due to fluorine radicals in both cases, Si:SiGe < 1 may be the result of either lower bond energy of Si-Ge compared to Si-Si, or band gap narrowing with Ge addition[1]. For Si:SiGe > 1, the etch rate of SiGe is inhibited with SF6 gas under the right process conditions, which may be due to preferential deposition of an involatile sulfur blocking layer [2]. This work demonstrates the range of selectivity and isotropic etch capabilities between Si and SiGe using RLSA$^{TM}$.

[1] S. Borel, V. Caubet, J. Bildea, A. Cherif, C. Arvet, C. Vizioz, J.M.Hartmann, G.

Rabillé and T. Billona. ECS Transactions, 3 (7) 627-642 (2006)

[2] G. S. Oehrlein, T. D. Bestwick, P. L. Jones, M. A. Jaso, and J. L. Lindstrorn. J. Electrochem. Soc. 138, 1443 (1991).

8:40am **PS-TuM3 Control of Anisotropic Simultaneous SiGe-Si Etching for Dual Channel Fin Applications**, ***Yohei Ishii***, *M. Walker, R. Scott-McCabe, A. Yu,* Hitachi High Technologies America, Inc., *K. Okuma*, Hitachi High-Technologies Corp., Japan, *K. Maeda, J. Sebastian, J. Manos*, Hitachi High Technologies America, Inc.

As a result of miniaturization by the semiconductor industry to follow the pace of Moore’s law, new design approaches to manufacturing have been introduced. Logic device structures have transitioned from traditional planar designs to three dimensional Fin-type Field Effect Transistors (FinFET). This structure change has achieved improved device characteristics such as higher drive currents and lower transistor leakage. To further enhance FinFET electrical performance, a potential approach is the use of high mobility channel materials such as silicon germanium.

In current fabrication schemes, achieving vertical fin profiles and controlling RIE lag are typical issues associated with the fin etch process. However, with the use of silicon in n-FETs and silicon germanium in p-FETs, new etching challenges such as material-dependent etching rate differences have emerged. During the fin etching process, the silicon and silicon germanium must now be etched simultaneously. Silicon germanium etching characteristics have been studied and the results indicate that, with conventional halogen chemistries, the etch rate of silicon germanium is greater than silicon [1]. Should future technology nodes adopt silicon-germanium as a high mobility channel material, etching processes must consider how to control these material-dependent phenomena.

In this presentation, we will introduce an etching process which can be used for dual channel SiGe/Si fin etching. The result shows that the etched amount difference between silicon germanium and silicon can be controlled from a positive value (silicon germanium etching rate is greater than silicon etching rate) to a negative value. Surface analyses were also utilized to further understand the process and the mechanism. Details will be discussed in this presentation.

[1] G.S. Oehrlein, Y. Zhang, G. M. W. Kroesen, E. de Fresart, and T. D. Bestwick, Appl. Phys. Lett. **58**, 2252 (1991)

9:00am **PS-TuM4 Etch Rate and Profile Tailoring of Si and $SiO_2$ through Laser-Stimulated Thermal Desorption**, ***Jason Peck***, *D.N. Ruzic*, University of Illinois at Urbana-Champaign

In this work, laser exposure was coupled with plasma etch processes for local etch rate enhancement (and under some conditions, etch activation). Materials were tested which are most-frequently used in semiconductor devices – namely Si, $SiO_2$, and Cu. A 100 Hz, 7 ns pulse width Q-switched Nd:YAG laser was applied at its 1064, 532, and 266 nm modes. Using the 532 nm line on Si (40 mJ/cm$^2$/pulse) with a radiofrequency inductively-coupled plasma (RF-ICP) source placed upstream, laser etch enhancement effect was 4 Å /s in 50:4 sccm Ar/$SF_6$, and 3 Å /s etch enhancement at 50:8:2 sccm Ar/$C_4F_8$/$O_2$. With no $O_2$ flow in a 50:8 sccm Ar/$C_4F_8$ chemistry in an RF capacitively-coupled plasma (RF-CCP) source with a measured self-bias of -140 V, etch activation was seen at 0.62± 0.07 W/cm$^2$ (6.2± 0.7 mJ/cm$^2$), with etch rates linearly increasing with laser intensity. The 266 nm line saw etch activation at roughly the same intensity, though etch rate scaling with laser intensity was roughly 6 times higher than 532 nm, corresponding to the drastically-larger absorption depth of 266 nm in Si. No etch enhancement was produced in either chemistry for $SiO_2$ due to its transparency across the UV-VIS-NIR spectrum, even at 266 nm. $CF_x$ polymer thinning was observed on both Si and $SiO_2$ at 266 nm but only on Si at 532 nm, indicating a thermally-driven desorption mechanism which relies on heating the material beneath.

It was shown that continuous wave (CW) laser sources of 405, 455, and 520 nm were unable to produce etch enhancement even up to intensities of 200 W/cm$^2$, demonstrating the necessity of rapid heating of the Q-switched Nd:YAG source (~10s of MW/cm$^2$ over 7 ns) to temporarily but drastically increase wafer surface temperature. COMSOL simulations showed that a Si surface over the duration of a 532 nm laser pulse would increase temperature by 2.7° C per mJ/cm$^2$ – a reliably linear rate, even at high intensity. Testing of highly-doped Si wafers revealed a substantial increase in etch enhancement – $10^{19}$ and $10^{21}$ cm$^{-3}$ P-doped wafers showed 1.7× and 3.7× higher etch rates over intrinsic Si, respectively. The increased absorption coefficient in these doped wafers confirmed that the etch enhancement mechanism was due to desorption of etch products through thermal heating, rather than through photolytic bond breaking.

Finally, etch tests of 100 nm full-pitch, 100 nm deep trenches showed the ability to tailor etch profile based on wafer orientation. Polarization parallel to the trench line enhanced etching at the top of the features, while perpendicular to the trench line increased trench bottom etch rate.

9:20am **PS-TuM5 Prediction and Control of Fluctuation of Etching Properties by Simulation Technology**, ***Nobuyuki Kuboi***, *M. Fukasawa, T. Tatsumi*, Sony Semiconductor Solutions Corporation, Japan **INVITED**

Fluctuations of etching properties such as the etched profile and damage distribution can affect the performance of advanced CMOS devices, making the prediction and control of these properties vital for mass production. However, the fluctuations mechanisms are not perfectly understood because of equipment limitations in the plasma monitoring systems used in mass production. Therefore, as a predictive technology, a plasma etching simulation was developed that considers the physical and chemical aspects of the plasma and the etched surface.

We modeled $CH_xF_y$ plasma for SiN etching with a CCP system, taking into account the interaction between the bulk region and the chamber wall surface, and simulated the hydrogen (H) density distribution and H Balmer line emission (virtual OES) [1][2]. From comparisons with experimental OES, the reaction probabilities of H with varying chamber wall conditions (Si, $SiO_2$, polymer) were derived as 0.5, 0.06, and 0.1, respectively. Using these values, the incident H radical flux was calculated, and found to correlate with the SiN etch rate. This signifies that flux fluctuation is important for controlling the SiN etch rate.

To predict the etched profile and damage distribution for SiN, $SiO_2$, and Si etching, we developed a new simulation technique using an extended 3D voxel model. This included a Slab model [3] that divides the surface region into several thin slabs and time-dependently solved the surface reactions of its reactive and deposition layers, as well as the depth. We demonstrated SiN sidewall (SW) etching for MOSFET and bulk FinFET with $CH_xF_y$ plasma, successfully describing the etching properties. In addition, a local damage distribution can be seen around the SW edge and in the Si fin, which is difficult to find by experimental analysis. Furthermore, our simulation found that a large amount of Si damage in the Si substrate is caused during $SiO_2$/Si contact hole etching despite the high $SiO_2$/Si selectivity (>20) [4], which also exhibits time-dependence. Also, fluctuations of the CD and the Si recess during Si gate etching by HBr/$O_2$ plasma are greatly affected by the byproduct ($SiBr_x$), exhibiting a dependence on the factor $(R_G+R_S)S$ that includes the wafer ($R_G$) and chip ($R_S$) open area ratios, and pattern solid angle ($S$) [5].

These simulation technologies give us useful knowledge for optimizing the chamber wall condition, plasma etching process, and pattern design for advanced CMOS devices.

[1] Kuboi *et al*., JJAP **49**, (2010) 08JD01.

[2] Fukasawa *et al*., JJAP **48**, (2009) 08HC01.

[3] Kuboi *et al*., JVST A **33**, (2015) 061308.

[4] Nakamura *et al*., JVST A **25**, (2007) 1062.

[5] Kuboi *et al*., JVST A **31**, (2013) 061304.

11:20am **PS-TuM11 Underlayer Impact on Line Width Roughness in Extreme Ultraviolet Lithography and Etch**, ***Indira Seshadri***, *A. DeSilva, Y. Mignot, W. Xu, L. Meli, J. Guo, S. Sieg, J.C. Arnold, N. Felix*, IBM Research Division

Extreme ultraviolet (EUV) lithography enables single expose patterning of fine-pitch features, eliminating the need for complex multiple patterning schemes. However, reduction of line width/line edge roughness (LER/LWR) to match multiple patterning is a fundamental challenge with EUV. Typical EUV patterning stacks consist of resist, hardmask and planarizing organic layer, and reduction of both the post-lithography resist LWR and the post hardmask etch LWR are key to achieving final feature targets. With EUV eliminating the requirement for reflectivity control, hardmask materials may be chosen based on high etch selectivity to resists, stack aspect ratio reduction and low defectivity (eg. Si-containing films). However, recent work[1,2] has shown that hardmask choice can significantly impact fundamental aspects of the lithography that are strongly correlated to LER/LWR, such as dose, process window and EUV secondary electron capture through interactions at the resist-hardmask interface. Here, we demonstrate the impact of different classes of hardmask materials on LWR in fine pitch metal line features, post litho and post etch. With three classes of hardmasks – Organic spin-on films, inorganic deposited Si-based films, and metal containing films, we first evaluate post lithography LWR with low and high sensitivity resists and dipole and quadrupole illumination shapes. We then characterize LWR after under layer open with optimal etch chemistries to reach target line/space sizes. With frequency analysis of LWR[3], we present fundamental mechanisms that explain the LWR trends arising from resist-illumination-hardmask interaction and etch based LWR smoothing for each class. Our results provide a key knob to aid hardmask selection to meet LWR targets for future nodes

1. A. DeSilva, I. Seshadri, A. Arceo, K. Petrillo, L. Meli, B. Mendoza, Y. Yao, M. Belyansky, S. Halle, N. Felix, “Study of Alternate hardmasks for extreme ultraviolet patterning”, J. Vac. Sci. Technol. B 36 (6), 2016.

2. D. De Simone, Y. Vesters,A. Shehzad, G. Vandenberghe, P. Foubert, C. Beral, D. Van den Heuvel M. Mao, F. Lazzarino, “Exploring the readiness of EUV photo materials for patterning advanced technology nodes,” Proc. SPIE 10143 (2017).

3. R. Bonam, C. Liu, M. Breton, S. Sieg, I. Seshadri, N. Saulnier, J. Shearer, R. Muthinti, R. Patlolla, H. Huang,” Comprehensive analysis of line-edge and line-width roughness for EUV lithography”, Proc. SPIE 10143 (2017).

11:40am **PS-TuM12 Patterning Challenges and Perspective Solutions for 5nm and Beyond**, ***Ying Zhang***, Applied Materials, Inc. **INVITED**

Patterning has imposed new challenges and opportunities to Etch, Film metrology. In a variety of multiple patterning schemes, such as Multiple Litho + Etch (LELE…), or Self-Aligned Multiple Patterning (SAxP), Edge Replacement Error (EPE) is approaching the limit, ~¼ of pitch, which will limit the continuing of pitch shrink [1]. The recent development of EUV technology and manufacturability will help to realize much needed complementary lithography technology [2]. The challenges of reducing EPE (< e.g., ~ ¼ pitch), pitch walking, and CD/CDU/LER/LWR controllability in <0.5 nm (3s ) regime have shifted from Lithography to Films, Etch and Metrology. Continuous improvements of current plasma etch and film technologies are facing challenges to carry out the tasks of multiple patterning for the industry to extend to 5nm. Can process fine tuning based on current plasma etch and film tool technologies accomplish the precision requirement of fabricating sub-20nm pitch patterning? Atomic Layer Deposition (ALD) technology has already played a key in self-aligned multiple patterning. Further exploring on ALD and gapfill technology to provide more films with conformal and gapfill capabilities are required to enable some highly challenging patterning schemes. Conceptually, Atomic Layer Etching (ALE) should be able to help, e.g., CD control, etch selectivity, etc. But the key question is how to realize true ALE. In this talk, some of the new developments, key challenges, and perspective solutions on processes, process integrations, and plasma etching and film systems for will be reviewed and discussed.

[1] Richard Schenker, Intel, SPIE 2016, Feb, 2016, San Jose, USA

[2] Yan Borodovsky, Intel, Leti Innovation Days, June 26th 2013, Grenoble, France

# 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.

**References**

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[2] P.Müller-Buschbaum; Adv. Mater. **26**, 7692-7709 (2014)

[3] A.Hexemer, P.Müller-Buschbaum; IUCrJ **2**, 106-125 (2015)

[4] P.Müller-Buschbaum; Polymer Journal (invited review) **45**, 34-42 (2013)

[5] S.Guo, M.A.Ruderer, M.Rawolle, V.Körstgens, C.Birkenstock, J.Perlich, P.Müller-Buschbaum; ACS Appl. Mater. Interfaces **5**, 8581-8590 (2013)

[6] W.Wang, S.Pröller, M.A.Niedermeier, V.Körstgens, M.Philipp, B.Su, S.Yu, S.V.Roth, P.Müller-Buschbaum; ACS Appl. Mater. Interfaces **7**, 602-610 (2015)

[7] C.M.Palumbiny, F.Liu, T.P.Russell, A.Hexemer, C.Wang, P.Müller-Buschbaum; Adv. Mater. **27**, 3391-3397 (2015)

[8] C.J.Schaffer, C.M.Palumbiny, M.A.Niedermeier, C.Jendrzejewski, G.Santoro, S.V.Roth, P.Müller-Buschbaum; Adv. Mater. **25**, 6760-6764 (2013)

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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[1] A. Wäckerlin, *et al.,* Nano Letters 17, 1956 (2017)

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].

[1] H.Y. Mao, Y.H. Lu, J.D. Lin, S. Zhong, A.T.S. Wee, W. Chen, Progress in Surface Science 88 (2013) 132.

Y.L. Huang, Y.F. Chen, W.J. Zhang, S.Y. Quek, C.H. Chen, L.J. Li, W.T. Hsu, W.H. Chang, Y.J. Zheng, W. Chen, A.T.S. Wee, Nature Comm. 6 (2015) 6298.

[2] Y.L. Huang, Z. Ding, W. Zhang, Y.H. Chang, Y. Shi, L.J. Li, Z. Song, Y.J. Zheng, D. Chi, S.Y. Quek, A.T.S. Wee, Nano Letters 16 (2016) 3682.

[3] Y.J. Zheng, Y.L. Huang, Y.F. Chen, W.J. Zhao, G. Eda, C.D. Spataru, W.J. Zhang, Y.-H. Chang, L.J. Li, D.Z. Chi, S.Y. Quek, A.T.S. Wee, ACS Nano 10 (2016) 2476.

[4] Z.B. Song et al., submitted.

## Surface Science Division
## Room: 25 - Session SS+HC-TuM

## Controlling Mechanisms of Surface Chemical Reactions

**Moderators:** Daniel Killelea, Loyola University Chicago, Andrew Teplyakov, University of Delaware

8:00am **SS+HC-TuM1 Multifunctional Adsorption on Ge(100)-2x1 Surface: The Role of Interadsorbate Interactions**, ***Tania Sandoval****, *S.F. Bent*, Stanford University

Adsorption of multifunctional molecules onto semiconductor surfaces provides a pathway to functionalize the surface while leaving unreacted functional groups available for reaction. These hybrid interfaces are important for applications in biosensors, microelectronics, and energy storage. These applications require homogeneous and controllable adsorption of these complex molecules. In this presentation, we will discuss two studies that help elucidate the driving forces governing the overall product distribution during adsorption of multifunctional molecules.

The first example describes the adsorption of homobifunctional pyrazine on the Ge(100)-2x1 surface. Pyrazine ($C_4H_4N_2$) is a six-membered ring molecule with two nitrogen atoms in the para position. The electron-rich nitrogen possesses a lone pair that can easily react with the surface through a dative bond. While benzene is not known to react with germanium, the addition of nitrogen to the aromatic ring opens up additional reaction channels. Previous studies of pyridine ($C_5H_5N$) on Ge(100) showed that reaction through the nitrogen can yield a mix of adsorption products. Our X-ray photoelectron spectroscopy (XPS) results suggest that pyrazine reacts with Ge(100)-2x1 to form a mix of reaction products. Analysis of the N(1s) and C(1s) spectra indicates that reaction of pyrazine occurs through the N-dative bond and via N=C and C=C cycloaddition reactions. The product distribution was found to be a function of temperature and coverage. This dependence suggests differences in the reaction channels as well as cooperative effects between adsorbate molecules.

The second example describes the adsorption of homotrifunctional 1,2,3-benzenetriol on Ge(100)-2x1 surface. 1,2,3-benzenetriol ($C_6H_6O_3$) is a trihydroxy phenol with three neighboring hydroxyl groups. The proximity between OH-groups promotes intra and inter-molecular hydrogen bonding. XPS and Fourier transform infrared spectroscopy results demonstrated that the reaction occurs through an OH-dissociative pathway. Coverage dependent shows that the extent of surface reactions per molecule decreases as the surface becomes crowded, and we predict this behavior is due to a combination of sterics and intermolecular hydrogen bonding. It has been previously shown that intermolecular hydrogen bonding can lower the reactivity of an OH group and prevent further reactions. Our theoretical analysis confirms that adsorbed molecules will preferentially interact with each other if unreacted OH groups are in close proximity. We expect that these interactions contribute to lowering the saturation coverage, as well as decrease the amount of dissociation events per molecule.

8:20am **SS+HC-TuM2 Steering the Chemical Reactions on Surfaces Toward Targeted Products**, *Q.T. Fan, T. Wang*, ***Junfa Zhu***, University of Science and Technology of China

The bottom-up construction of low-dimensional macromolecular nanostructures directly on a surface is a promising approach for future application in molecular electronics and integrated circuit production. However, challenges still remain in how to control the reaction pathways toward the formation of targeted nanostructures or dimensions. In this presentation, I will report our recent studies on the on-surface synthesis of low dimensional organic nanostructures on different substrate surfaces. These studies were performed under ultra-high vacuum (UHV) conditions using a combination of scanning tunnelling microscopy (STM), low energy electron diffraction (LEED) and high-resolution X-ray photoelectron spectroscopy (HR-XPS). Several examples will be shown to demonstrate that by employing different substrate templates,[1-4] special high-dilution synthesis condition[5] or hydrogen bond protection with dedicated precursor molecules on surfaces[6], surface reactions can be driven with different pathways towards the desired products. For example, on Cu(111) and Cu(110), after depositing the same precursor molecule, 4,4''-dibromo-meta-terphenyl (DMTP), at elevated temperatures, Ullmann coupling reaction can proceed via different pathways to form different nanostructures.[1-3] While on the Cu(110)-(2x1)O surface, by controlling the width of the Cu stripes, the spatial confinement effect can steer the reaction of DMTP to form either 1D zigzag organometallic oligomeric chains with different lengths or organometallic macrocycles with different widths.[4] More interestingly, when recently we transplanted the (pseudo-) high dilution method in solution to the conditions of on-surface synthesis in UHV, we found that the reaction of DMTP on Ag(111) can be tailored to specially form cyclic hyperbenzene with high-yield (84%) in contrast to the commonly formed zig-zag open-chain polymers.[5] Except for the presentation of these different structures on surfaces, we will also discuss the principles and mechanisms behind.

*This work is supported by the National Natural Science Foundation of China (21473178) and the National Basic Research Program of China (2013CB834605)*

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(6) Wang, T.; Lv, H.; et al., *Angew. Chem. Int. Ed.* **2017**, *56*, 4762.

8:40am **SS+HC-TuM3 Spectroscopic Characterization of Reaction Pathways over a Pd-Cu(111) Single-Atom Alloy**, *C.M. Kruppe*, ***Michael Trenary***, University of Illinois at Chicago **INVITED**

Low coverages of catalytically active metals deposited onto less active metal surfaces can form single atom alloys (SAAs), which often display unique catalytic properties. Such alloys are particularly attractive for selective hydrogenation reactions. It is therefore of interest to probe the surface structure and chemistry of such alloys in the presence of gas phase reactants. We have used polarization dependent reflection absorption infrared spectroscopy (PD-RAIRS) to monitor the in-situ hydrogenation of acetylene to ethylene over a Pd/Cu(111) SAA surface. The coverage and morphology of the deposited Pd is characterized with Auger spectroscopy (AES), temperature programmed desorption (TPD) of $H_2$ and CO, and PD-RAIRS of CO. After exposing clean Cu(111) and Cu(111) with various Pd coverages to 10 L of CO at 100 K, the RAIR spectra show that the surface is largely unchanged by the presence of less than 0.5 ML of Pd. In the presence of $1\times10^{-2}$ Torr of CO at 300 K, significant CO coverages are only achieved when Pd is present on the surface. The Pd coverage determined from CO peak areas obtained with RAIRS yields a value lower by about a factor of two than the Pd coverage obtained with AES. This is attributed to the presence of both surface and subsurface Pd, with only the former detectable by RAIRS of CO, but both detectable with AES. Surface species and gas phase products of $C_2H_2$ hydrogenation are monitored between 180 and 500 K on clean Cu(111) and Pd/Cu(111). With a total pressure of 1 Torr and a $C_2H_2$:$H_2$ ratio of 1:100, annealing a SAA-Pd/Cu(111) surface to 360 K results in complete conversion of all gas phase $C_2H_2$ to gas phase ethylene ($C_2H_4$), without producing any gas phase ethane ($C_2H_6$). The hydrogenation reaction is accompanied by acetylene coupling reactions that occur both on clean Cu(111) and on Pd-Cu(111).

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* **Morton S. Traum Award Finalist**

9:20am **SS+HC-TuM5 Reactivity of Pt and Rh Adatoms, Dimers, and Small Clusters on $Fe_3O_4$ (001)**, ***Jan Hulva††***, TU Wien, Austria, *M. Meier*, University of Vienna, Austria, *M. Setvin, Z. Jakub, R. Bliem, M. Schmid, U. Dieblod*, TU Wien, Austria, *C. Franchini*, University of Vienna, Austria, *G.S. Parkinson*, TU Wien, Austria

The rapidly emerging field of "single-atom catalysis" aims to drastically reduce the amount of precious metal required to catalyze chemical reactions by replacing nanoparticles with single-atom active sites. Although there are now many reports of active single-atom catalysts [1], the concept itself remains controversial because it is challenging to characterize real catalysts and determine the reaction mechanism. In our work, we study fundamental properties of supported single metal atoms using a surface science approach. We employ the $Fe_3O_4$ (001) surface as a model support, because it can stabilize dense arrays of single metal atoms to temperatures as high as 700 K [2,3]. In this contribution, we address the adsorption behavior and reactivity of the Pt and Rh adatoms, dimers, and small clusters using a combination of atomically resolved STM and non-contact AFM, high-resolution spectroscopy, and density functional theory. We conclude that Pt adatoms are inactive because CO adsorption results in mobility, and rapid sintering into $Pt_2$ dimers [5]. Pt dimers, on the other hand, are stable, and highly efficient CO oxidation catalysts. By isotopically labelling the oxide surface with $^{18}O$, we unambiguously show that a Mars van Krevelen mechanism is responsible for the catalytic activity. Rh adatoms interact more strongly with the oxide, and do not sinter upon adsorption of CO. As a result, we find that Rh adatoms do catalyze CO oxidation, also via an MvK mechanism.

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[2] – Phys.Rev.Lett.108(2012): 216103

[3] – Science 346 (2014): 1215-1218.

[4] – Angew. Chem. Int. Ed. 54.47 (2015): 13999-14002.

[5] – PNAS 113.32 (2016): 8921-8926.

9:40am **SS+HC-TuM6 An AP-XPS Study to Investigate the Reaction Mechanism of the Oxidation of CO on $Pt/TiO_2$ Nanoparticles: A Step Towards Closing both the Pressure and the Materials Gap**, ***Randima Galhenage***, *J.P. Bruce, D. Ferrah*, University of California Irvine, *I. Waluyo, A. Hunt*, Brookhaven National Laboratory, *J.C. Hemminger*, University of California Irvine

Platinum supported on oxides, such as $TiO_2$, are widely studied catalysts to drive oxidation reactions. Even though there are fundamental studies that have been done on single crystal Pt and $TiO_2$ to understand the reactivity and the mechanism, there lies a sizable knowledge gap due to the complexity of the real catalytic systems compared to the single crystal studies. We studied CO oxidation on a unique model system where Pt nanoparticles (NPs) are deposited on $TiO_2$ NPs supported on an inert HOPG surface. Our study takes the complexity of the material a step forward. In-operando Ambient Pressure X-ray photoelectron spectroscopy (AP-XPS) was used to study the oxidation states of Pt, Ti, and O during the reaction to understand the role of different oxidation states of the elements on the reaction mechanism. Ex-situ prepared model catalyst which mostly contains a mixture of Pt(4) and Pt(2) were first heated to obtain a mixture of Pt(0) and Pt(2). During the reaction, the $TiO_2$ remains stoichiometric with no indication of any change in the oxidation state. At 400 K, CO is adsorbed on Pt resulting in a decrease of the Pt(2)/Pt(0) ratio. O1s spectra show the formation of Pt-O bond at 450 K. A rapid decrease of O1s (Pt-O) and a decrease of Pt(2)/Pt(0) ratio were observed simultaneously with $CO_2$ production at 500 K. In conclusion, we were able to study CO oxidation on a more complex model system of $Pt/TiO_2$ and followed the reaction mechanism. CO first adsorb on Pt and reacts with the oxygen that is dissociated on Pt sites which agree with the existing Langmuir–Hinshelwood (LH) mechanism. Furthermore, we found out that CO gets adsorbed on Pt(2) rather than on Pt(0) when there is a mixture of Pt(2) and Pt(0).

11:00am **SS+HC-TuM10 Oxygen Reduction Reaction of Graphite Decorated by the Pyridinic-Nitrogen Contained Molecules with High Density**, ***Riku Shibuya***, *T. Kondo*, University of Tsukuba, Japan, *J. Nakamura*, University of Tsukuba, Japam

Nitrogen containing carbon materials have been reported to show catalytic activities such as an oxygen reduction reaction (ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) was found to create ORR active sites in our previous work [1]. We then try to prepare catalytically active carbon surfaces covered with pyridinic nitrogen-containing aromatic molecules with high density. Here we report model catalyst studies using HOPG (highly oriented pyrolytic graphite) electrode covered with pyridinic nitrogen-containing aromatic molecules (dibenz[a,c] acridine (DA) molecule). The DA molecules were deposited on HOPG with different coverage by simply dropping solutions of the DA molecules at room temperature. Scanning tunneling microscopy (STM) measurements revealed that a well-ordered two-dimensional structure of DA monolayer is formed on HOPG surfaces with high densities via $\pi$-$\pi$ interaction, rather than aggregates to form three-dimensional clusters. The nitrogen concentration of the DA-covered HOPG surfaces was estimated to be 0.5~1.5 at.% by XPS. The DA-covered HOPG model catalysts reveled activities of ORR. The specific activity per pyridinic nitrogen atom was estimated to be 0.08 (e $sec^{-1}$ $pyriN^{-1}$) at 0.3 eV, which is comparable to that for pyridinic nitrogen incorporated graphene sheets (0.07 ~ 0.14 (e $sec^{-1}$ $pyriN^{-1}$))[1]. The current densities at 0.1, 0.2, and 0.3 V vs RHE were in proportional to the surface coverage of DA molecules, indicating that the ORR active site was created by DA molecule adsorbed on HOPG. The present studies clearly show that fixing nitrogen-containing aromatic molecules on graphitic carbon materials is one of promising approaches to prepare active ORR carbon catalysts.

References

[1] D.Guo, R.Shibuya, T.Kondo, J.Nakamura, et al., Science, 351 (2016), 361-365.

11:20am **SS+HC-TuM11 Spectroscopic and Computational Studies of Room-Temperature Decomposition of a Chemical Warfare Agent Simulant on Copper Oxide**, ***Lena Trotochaud***, Lawrence Berkeley National Laboratory, *R. Tsyshevsky, S. Holdren*, University of Maryland, College Park, *K.P. Fears*, U.S. Naval Research Laboratory, *A.R. Head*, Lawrence Berkeley National Laboratory, *Y. Yu*, University of Maryland, College Park, *O. Karslioglu*, Lawrence Berkeley National Laboratory, *S. Pletincx*, Vrije Universiteit Brussel, Belgium, *B. Eichhorn*, University of Maryland, College Park, *J. Owrutsky, J. Long*, U.S. Naval Research Laboratory, *M. Zachariah, M.M. Kuklja*, University of Maryland, College Park, *H. Bluhm*, Lawrence Berkeley National Laboratory

Filtration systems for absorption and decomposition of chemical warfare agents (CWAs) are the first line of defense against exposure to these toxic compounds. Composite materials (such as ASZM-TEDA) commonly used in filtration systems consist of high-surface-area carbon supports impregnated with various metal oxides, including $CuO_x$. Despite decades of work to develop highly effective and versatile filtration materials, little is known about the mechanisms of CWA degradation by material surfaces and filter deactivation/poisoning, in part due to the challenges involved with spectroscopic characterization of filtration material surfaces under operating conditions. Enabling the rational design of more advanced filtration and decomposition materials for broad-spectrum protection against CWAs and other toxic industrial compounds requires a sophisticated understanding of the chemical mechanisms behind CWA sorption and degradation on the molecular scale.

We will present work detailing the mechanism of adsorption and decomposition of dimethyl methylphosphonate (DMMP), a CWA simulant, on polycrystalline copper oxide surfaces. Ambient-pressure XPS enables examination of these surfaces and adsorbed species upon exposure to DMMP and other common atmospheric gases, such as water vapor and $NO_x$. Multiple decomposition products are observed on $CuO_x$ surfaces, and the oxidation state of the metal appears to influence the mechanistic pathway. Complementary density functional theory (DFT) and *in situ* FTIR studies corroborate our experimental findings and are used to propose likely decomposition pathways. Exposure of the $CuO_x$ surfaces to water vapor or $NO_x$ prior to introducing DMMP affects the decomposition product distribution, but does not appear to significantly inhibit the initial DMMP adsorption.

11:40am **SS+HC-TuM12 Atomic View of Acid Zeolite Chemistry: Surface Chemistry Studies on 2D Silicate Materials**, ***Jin-Hao Jhang***, *G.S. Hutchings, C. Zhou, U.D. Schwarz, E.I. Altman*, Yale University

Although zeolites have been used in facilitating numerous catalytic reactions for decades, it is still a long-term challenge to understand how surface properties of zeolites promote catalytic reactions. Recently, two-dimensional (2D) silicate materials were discovered and prepared successfully on different substrates, including transition metals and alloy. This achievement makes surface science approaches possible for understanding zeolite chemistry from an atomic view. In this work, we seek to establish that 2D silicates are capable of promoting acid catalyzed reactions in a manner analogous to 3D zeolites. The 2D silicates were prepared on a Pd(111) substrate via physical vapor deposition (PVD) at room temperature followed by annealing at 1000 K in an oxygen background. The probe molecule 2-propylamine reacts through a deammination process and produces propene on the 2D aluminosilicate indicating the existence of acid sites capable of catalysis. In contrast, no propene or other products were detected on the 2D silica surface. We also generated atomic deuterium (D) on both silica and aluminosilicate by a $D_2$-plasma treatment and a $D_2$-recombination feature at 540 K assigned to the decomposition of surface OD groups was only observed from the aluminosilicate sample. These findings show the similarity between the 2D aluminosilicate and the acid zeolites which allows us to consider the 2D material as a zeolite model to explore zeolite chemistry.

12:00pm **SS+HC-TuM13 Establishing Rules for Oriented SURMOF Growth Beyond Template Effects**, *X.-J. Yu*, University of Frankfurt, Germany, *J.-L. Zhuang*, Guizhou Normal University, P.R. China, ***Andreas Terfort***, University of Frankfurt, Germany

The surface deposition of metal-organic frameworks (MOFs) opens the opportunity to use these highly designable materials for applications in electronics, data storage, sensing or biointerfaces. Several protocols have been reported to grow or attach MOFs onto a variety of surfaces, but nevertheless, the bandwidth of successfully deposited MOFs is still extremely limited: Besides the archetypical HKUST-1 and ZIF-5, only a family of tetragonal layer systems (with or without pillars) could be grown into well-defined SURMOF layers [1]. Although with some of these systems impressive results for different devices, such as photovoltaic cells, have been reported, the limitation to these classes of MOFs is unsatisfactory.

In this talk, we wish to discuss that the lack of success with other systems is related to the fact that most projects relied solely on the well-established surface-template effects, in which the coordination of surface-bound, functional groups to the metal SBU defines not only the binding mode but the orientation of the whole film. We will show that the rules on the surface differ from the ones in solution by a reduced number of trajectories, which in turn hamper certain reactions [2]. It is also of importance to keep in mind the different surface energies of the crystal surfaces, which can dictate a reorientation of the preformed system by Ostwald ripening during the deposition process [3]. All these processes involve different activation energies, the careful control of which opens the opportunity to grow well-oriented films of MOF systems, which have behaved notoriously difficult up to now.

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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.

## Thin Films Division
## Room: 20 - Session TF-TuM

## Advanced CVD and ALD Processing, ALD Manufacturing and Spatial-ALD

**Moderators:** Halil Akyildiz, Uludag University, Turkey, Paul Poodt, Holst Centre / TNO, Netherlands

8:00am **TF-TuM1 Aluminum-Doped Zinc Oxide via Spatial ALD: Process Impact on Film Morphology, Electrical Conductivity and Stability**, *S.F. Nelson*, ***Lee Tutt***, *C.R. Ellinger*, Eastman Kodak Company

Aluminum-doped zinc oxide (AZO) is an attractive transparent conductive material because of to its nontoxic, earth-abundant material composition. A wide range of electrical properties have been reported for AZO deposited using a variety of techniques and a range of process conditions. This talk will focus on the AZO grown using spatial atomic layer deposition (SALD), and the impact of process conditions on the electrical, optical and crystallographic properties of the resultant AZO films. We will report primarily on those AZO films deposited using a co-flow of dimethyl aluminum isopropoxide (DMAI) and diethyl zinc (DEZ) as the metal precursors, and water as the oxygen source.

We will share our current understanding of the mechanisms responsible for the interplay between process parameters and material properties, including the correlation of film properties such as doping-level and crystallographic structure to the end-use properties of conductivity and optical transparency. For reference, we have deposited AZO having a bulk resistivity of $2.7 \times 10^{-4}$ Ω-cm and an average visible transmission of 85%, obtained from 204 nm thick AZO films deposited at 300°C. This compares well to commercially available ITO coatings having, for example, about $1.2 \times 10^{-4}$ Ω-cm and 82% average visible transmission for film thicknesses between 150 nm and 200 nm.

In addition, the impact of passivating the AZO surface with very thin aluminum oxide ($Al_2O_3$) will also be reported. We have found that passivation with $Al_2O_3$ enhances conductivity through an increase in both mobility and carrier concentration. Improved thermal stability during elevated annealing conditions in air was also observed for alumina-passivated AZO samples

8:20am **TF-TuM2 Fast Pulsing of Precursor and Reactant to Merge ALD and CVD Processes: Example of Thick $Al_2O_3$ Deposition**, ***Fabien Piallat***, *L. Bonnet, J. Vitiello*, KOBUS, France

A specific pulsed-CVD reactor was developed for the chemically enhanced deposition of materials. In this specific reactor, both reactant and precursor can be pulsed or sent continuously to the deposition chamber. Thus, many materials can be deposited by one of the three following methods, Atomic Layer Deposition (ALD), Chemical Vapor Deposition (CVD) or pulsed-CVD.

In this presentation, an investigation of $Al_2O_3$ deposition will be presented, with detailed process comparison for each of the three techniques in order to highlight the variability brought by the process on the material properties. $Al_2O_3$ deposition was done with TriMethylAluminium (TMA) precursor and $O_2$ in-situ plasma.

Influence of the pulse length on the deposition rate shows a gap between the surface saturation growth mode of the ALD and the continuous growth of the CVD. Starting with pulse length in the order of seconds, in the case of the ALD mode, a reduction of the pulse length leads first to a reduction of the growth rate, because the precursor does not have enough time to adsorb at the sample surface to form a monolayer. Then, in a second time, for pulse time in the order of hundreds milliseconds, there is an increase of the growth rate, due to the change in the growth mode, from the surface saturation to the continuous growth. Further reduction of the pulse length, in the order of tens milliseconds, the growth can be assimilated to a CVD growth, with properties similar to the one of material obtained in continuous growth.

Additionally, extraction of the activation energy of the deposition reaction, using the Arrhenius law from deposition at temperature ranging from 100°C up to 450°C, will give some insight on the importance of the process on the favoring of the deposition reaction.

Finally, to address the photonic and MEMS applications, thick layers of $Al_2O_3$ will be deposited by the three methods and will be characterized by ellipsometry, Fourrier Transformed Infra-Red (FTIR), Raman measurement and X-ray Diffration (XRD). Pro and cons of each technique will be discussed based on these characterizations.

8:40am **TF-TuM3 Employing Atmospheric Pressure Micro-Plasma Printer for ALD of $TiO_2$ Thin Films**, ***Morteza Aghaee***, *J. Verheijen*, Eindhoven University of Technology, The Netherlands, *A. Stevens*, InnoPhysics B.V., The Netherlands, *W.M.M. Kessels, M. Creatore*, Eindhoven University of Technology, The Netherlands

A broad range of devices such as thin film transistors (TFTs), solar cells, sensors and microfluidic channels benefit from micron-scale patterns in their structure. These micron-scale patterns are often fabricated by means of costly methods such as (photo-)lithography. For this reason, there is a large interest in alternative simple and cost-effective approaches for micron-scale to sub-millimeter patterning that reduce the number of etch and lithography process steps.

A micro-plasma printer [1], which is based on a unique needle-to-plate micro-plasma dielectric barrier discharge (DBD), has recently been developed for spatially-resolved surface functionalization [2] and deposition of organic films [3] with sub-millimeter range resolution. In this contribution, the potential of the micro-plasma printer in delivering patterned, ultra-thin inorganic films at atmospheric pressure is addressed. Specifically, the setup is adopted to carry out thin film $TiO_2$ deposition in two configurations, namely plasma enhanced chemical vapor deposition (PE-CVD) and plasma-assisted atomic layer deposition (PA-ALD).

The properties of the $TiO_2$ layers as well as the patterning resolution have been investigated. The $TiO_2$ films deposited by PE-CVD mode have not shown satisfactory results in terms of purity and density of the layers (more than 5% C and refractive index of 1.8). However, the PA-ALD mode has been able to deliver patterns of amorphous $TiO_2$ films with low level of impurity and sub-nanometer thickness control. A growth rate of 0.15 nm/cycle has been obtained for 500 ms and 400 µs of TTIP and $N_2/O_2$ plasma exposures in each PA-ALD cycle, respectively. Rutherford backscattering spectroscopy (RBS) has revealed a growth rate of 2.4 Ti atoms per nm$^2$.cycle in saturation condition. Improvement of density and reduction of film impurities (H, C and N content) have been observed by prolonging the plasma exposure time. $TiO_2$ films with refractive index of 2 and less than 1% C have been deposited by 2 ms of plasma exposure. The width of the smallest features deposited by PE-CVD and PA-ALD modes have been determined by XPS line scan measurements to be 1.8 mm and 900 µm, respectively, for 7 nm thick layers.

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[3] J.R.G Schalken, M. Creatore, P. Verhoven, A. Stevens, Nanoscience Nanotechnol. Letter, 7 (2015) 62-66.

9:00am **TF-TuM4 Large-Area Atmospheric Pressure Spatial ALD**, *C. Frijters, F. van den Bruele, F. Grob, **Paul Poodt***, Holst Centre / TNO, Netherlands

Atmospheric spatial ALD (sALD) is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. First industrial applications of Spatial ALD include passivation of c-Si solar cells and roll-to-roll manufacturing of flexible barrier foils. An emerging application for Spatial ALD are flat panel (OLED) displays. We have developed spatial ALD processes for making high mobility oxide semiconductors for the TFT backplane as well as thin-film encapsulation for the OLED front plane. As today's displays are fabricated using glass panels in the order of several square meters, a remaining challenge is the development of large-area sALD deposition technology that is able to combine high throughput with uniform performance across large areas.

As an intermediate step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm$^2$ sized substrates, able to deposit uniform films across a deposition width of 300 mm. The whole tool is operated under an atmospheric but inert N$_2$ atmosphere. We will present the basic deposition performance of the tool, where large-area thickness non-uniformities of less than 1% have been achieved for alumina on glass. Furthermore, we will demonstrate excellent compositional uniformity for binary oxides.

One of intended applications is thin-film encapsulation of OLED devices. In order to test the encapsulation performance of the films deposited by the large area spatial ALD tool, we deposited single layer and double layer alumina films, in combination with printed organic planarization layers, on PET foils laminated on 325 mm x 325 mm glass panels. The encapsulation performance was tested under damp-heat conditions. The deposited encapsulation stacks show excellent results, with virtually no visible defect appearing after more than 1000 hrs. at 60 °C 90 %RH, corresponding to a potential device lifetime of at least 2.5 years. These results demonstrates the potential of spatial ALD for manufacturing large-area OLED devices.

9:20am **TF-TuM5 High Speed ALD of Multifunctional ALD Ultrabarriers for Flexible OLED Encapsulation**, ***Jacques Kools***, Encapsulix, France **INVITED**

In recent years, Atomic Layer Deposition (ALD) has established itself as a viable technology for deposition of ultrabarriers on large area electronic devices such as photovoltaics, OLED's and organic electronics. As a first generation material, Alumina ( Al2O3) has been established as the workhorse material to deliver excellent water vapor and oxygen barrier properties. However, many devices require protection from a multitude of invasive fluxes, such as UV light, salt water, electromagnetic radiation, ... etc. A nanoengineered synthetic barrier material allows to tune the different physical properties of the barrier.

In this paper we will describe our recent work on the development of hardware and process for industrial deposition of nanoengineered barriers, with properties that have been optimized to the specific device requirements. Leveraging the unique ability of ALD to control materials on the atomic scale, multilayered barriers are constructed atomic layer by layer from a set of up to ten precursor materials. In this way, it is possible enhance the flexibility ( by the use alucone layers), the UV resistance ( by the use of TiO2), the resistance to liquid water.. etc.

Process development and manufacturing experience in the OLED industry will be discussed.

11:00am **TF-TuM10 Simulation of Atomic Layer Deposition**, ***Paul Moroz***, TEL Technology Center, America, LLC, *D. Moroz*, Harvard University

Semiconductor industry overcomes many challenges by advancing materials processing to new levels of precision, accuracy, manufacturability, and reliability, while the role of numerical simulations grows. Here we present new results on Monte Carlo feature-scale simulations of Atomic Layer Deposition (ALD) conducted with a feature-scale simulator, FPS3D [1-5], as well as comparison of obtained simulation results with corresponding experiments. The ALD processes are often complex, involving large molecules and, to our knowledge, have not been addressed by other feature-scale simulations except via FPS3D [4-5]. ALD has a potential for conformal and precise deposition. However it requires definite conditions for being successful, and those conditions are very important to understand. The main factor of all of ALD schemes is the cyclic change of flux parameters and the corresponding chemistry, producing a single monolayer or, most typically, a fraction of a monolayer of the deposited film after application of a cycle. We consider two very different cases of SiN film deposition. The first one uses cycles of dichlorosilane and ammonia plasma, while the second one applies cycles of disilane and hydrazine. The SiN deposition rate for the former corresponds to a half of a monolayer per cycle, while for the later, it saturates at values close to a full monolayer per cycle. Steric hindrance was found to be an important factor in explaining those phenomena.

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[4] P. Moroz, 15th Int. Conf. on Atomic Layer Deposition, Portland, OR (2015).

[5] P. Moroz, D. J. Moroz, to be published in Japan. J. of Appl. Physics (2017).

11:20am **TF-TuM11 Boron Nitride Film Growth at Room Temperature Using Electron Enhanced Atomic Layer Deposition (EE-ALD)**, ***Jaclyn Sprenger***, *H. Sun, A.S. Cavanagh, S.M. George*, University of Colorado Boulder

Electron-enhanced atomic layer deposition (EE-ALD) can drastically reduce the temperatures required for film growth. The temperature reduction occurs because electrons can desorb surface species by electron stimulated desorption (ESD) to create very reactive "dangling bonds". Precursors can then adsorb efficiently on the dangling bonds. EE-ALD lowers the thermal budget and enables the deposition of thin films on thermally sensitive substrates. EE-ALD has been demonstrated previously for the deposition of polycrystalline GaN [1] and amorphous Si [2] at room temperature.

BN film growth by EE-ALD was performed at room temperature on Si (111) substrates using alternating doses of borazine (B$_3$N$_3$H$_6$) and low-energy electrons. Borazine is a single-source precursor for BN deposition. *In situ* ellipsometry was performed during the BN EE-ALD. These ellipsometry measurements yielded a linear growth rate of ~3 Å/cycle for electron energies of 100 eV with an electron current of 300 µA for 240 s. This *in situ* growth rate was confirmed by *ex situ* spectroscopic ellipsometry. A BN film with a thickness of 150 nm was deposited after ~500 EE-ALD cycles (see supplemental Figure 1). *Ex situ* ellipsometry measurements show flat BN thickness spatial profiles (see supplemental Figure 2) which are consistent with self-limiting reaction conditions including hydrogen desorption.

Film composition was studied with *ex situ* XPS (see supplemental Figure 3). The BN composition is consistent throughout the film with a B/N ratio of 1.3/1. The films are pure with C and O concentrations of only <3 at.% in the bulk of the film. A thin, self-passivating surface oxide resulting from atmospheric exposure is present. In addition, *ex situ* FTIR transmission was performed on the BN films. These FTIR measurements yielded an absorption peak at ~1370 cm$^{-1}$ that is consistent with hexagonal BN.

[1] J.K. Sprenger, A.S. Cavanagh, H. Sun, K.J. Wahl, A. Roshko and S.M. George, "Electron Enhanced Growth of Crystalline Gallium Nitride Thin Films at Room Temperature and 100°C Using Sequential Surface Reactions", *Chem. Mater.* **28**, 5282 (2016).

[2] J.K. Sprenger, A.S. Cavanagh, H. Sun and S.M. George, "Electron Enhanced Atomic Layer Deposition (EE-ALD) of Silicon Films at Room Temperature", Presentation at ALD2016 in Dublin, Ireland.

11:40am **TF-TuM12 CVD of sp$^2$-BN on Si(111) Substrates**, ***Laurent Souqui***, *H. Pedersen, H. Högberg*, Linköping University, Sweden

Boron nitride (BN) is a wide bandgap semiconductor related to the other 13-nitrides (or III-nitrides), aluminium nitride (AlN) or gallium nitride (GaN). As BN is isoelectronic to carbon, it demonstrates graphite-like structure (sp$^2$-BN) in hexagonal BN(h-BN) and rhombohedral BN, (r-BN). In addition, BN exists as disordered phases such as amorphous (a-BN) or turbostratic (t-BN). Crystalline h-BN and r-BN films are promising materials for application such as UV-devices, power electronics and neutron detectors. Furthermore the similarities between graphene and sp$^2$-phases such as h-BN and r-BN make BN a commensurate insulating growth template for graphene.

Our previous works were focused on the CVD of epitaxial sp$^2$-BN films on Al2O3(0001) and 6H-SiC(0001) substrates [1] and found the optimal condition for BN growth to be around 1500°C. We now study the growth of boron nitride on silicon substrates (Si) as silicon is cheap, abundant and is a mature technology. However, due to its low melting point (1414°C), Si cannot withstand such high temperature processes. Because of the necessity of growing at lower temperature, CVD BN films grown on silicon usually show low crystallinity i.e. often a-BN, t-BN or nano-crystalline BN.

In this work, thin BN films were grown on Si(111) substrates in a horizontal hot-wall CVD reactor. Triethylborane (TEB) and ammonia ($NH_3$) were used as precursors and reacted at temperatures between 1200°C and 1300°C. The substrates were in-situ annealed in silane ($SiH_4$) and $NH_3$ before the deposition. Further, a small fraction of $SiH_4$ was also introduced during the growth as this has been shown to favour growth of crystalline $sp^2$-BN films [2]. Fourier-Transform Infra-Red spectroscopy (FTIR) confirms the presence of $sp^2$-BN. Adjustment of the $SiH_4$ concentration in the growth flux results in the deposition of crystalline films attributed to $sp^2$-BN in X-ray diffraction. In contrast, films deposited on Si at the same conditions but without $SiH_4/NH_3$ pre-treatment hardly nucleates and is amorphous to X-rays. This shows the importance of surface preparation in order to grow crystalline BN films on Si. In addition to growth of boron nitride, we observe the growth of SiC grains either due to a reaction between alkyl by-products from TEB and either the substrate or $SiH_4$ from the gas phase.

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[2] M. Chubarov, H. Pedersen, H. Högberg and A. Henry, CrystEngComm, 2013, 15, 455.

12:00pm **TF-TuM13 Microcontroller-based Sequential Deposition Control Systems using Behavior Tree Algorithms: ALD for the "App Generation"**, ***Brandon Piercy***, *J. Crane, M.D. Losego*, Georgia Institute of Technology

A major challenge for researchers developing custom deposition equipment is the design and creation of the control software and electronics. While a simple loop-based control logic is often sufficient for sequential deposition applications like atomic layer deposition (ALD), it becomes cumbersome and difficult to reprogram when integrating more complex functionality or decision making. Furthermore, there are limited examples of publicly available control code or hardware schematics that can be easily integrated into an existing system. The "behavior tree" algorithm, developed in the robotics and artificial intelligence communities, is a highly adaptable and intuitive method to create complex behaviors. With behavior trees, we have created unique deposition recipes that would be challenging to implement using simpler control algorithms. We have written the core algorithm to run on widely available microcontrollers, making it possible to control equipment remotely using mobile "apps" or a centralized computer. In this talk, we will describe our microcontroller implementation and how it can be rapidly integrated into new or existing sequential deposition systems.

## Vacuum Technology Division
## Room: 7 & 8 - Session VT-TuM

### Large Vacuum Systems
**Moderators:** Jason Carter, Argonne National Laboratory, Gerardo Brucker, MKS Instruments, Inc., Pressure and Vacuum Measurement Group

8:00am **VT-TuM1 The Role of Vacuum Technology in Discovering the Gravitational Waves from Merging Black Holes**, *R.F.M. Weiss*, ***Michael Zucker***, LIGO Project Caltech and MIT **INVITED**

The observation of the gravitational waves from the merger of two black holes involved measuring the motion of mirrors to a precision of $10^{-18}$ meters over a distance of 4 km. The measurement was made by optical interferometry between suspended mirrors. Vacuum of $10^{-9}$ torr was required in 1.2 meter diameter 4km long beam tubes to avoid phase noise of the light and equivalently high vacuum was needed to avoid thermal noise of the mirrors from molecular collisions. The residual hydrocarbon background had to be controlled to avoid contamination of the optics. A significant challenge was to design and construct the vacuum system economically. Some of the fundamental physics and the engineering of the system will be described.

8:40am **VT-TuM3 Vacuum System Engineering for Cornell Brookhaven ERL Test Accelerator**, ***Yulin Li***, *D.C. Burke, B. Johnson*, Cornell Laboratory for Accelerator-Based Sciences and Education

A novel electron accelerator, Cornell Brookhaven ERL Test Accelerator (CBETA), is under development by a collaboration between Cornell Laoratory of Accelerator-based Sciences and Education (CLASSE) and Brookhaven National Laboratory. As a prototype accelerator for eRHIC, many unique accelerator technologies will be tested in CBETA, including photo-cathode electron injector, 4-turn superconducting RF (SRF) Energy Recover LINAC (ERL), non-scaling Fixed-Field Alternating Gradient (NS-FFAG) optics with 4x energy acceptance. The CBETA layout consists of an existing photo-cathode injector with SRF cryomodule (ICM) and a main LINAC cryomodule (MLC), a NS-FFAG return loop that transports electron beams at four energies, 42, 78, 114 and 150 MeV in single bore beampipe, and two splitter sections where the four energy beams are separated. The total circumference of CBETA loop is about 80-m. The basic requirement of CBETA vacuum system is to achieve adequate level of vacuum and physical aperture for transporting electron beams at four different energies. Furthermore, by the nature of test accelerator, the vacuum system engineering must accommodate a very high density of beam diagnostics tools, such as 100+ beam position monitors, beam profile viewers, etc. Beam path length up to 20° RF-phase is required in the splitter sections. Aluminum alloy is chosen for beampipe construction material for its good electric conductivity (resistive-wall), no residual radioactivity (from beam losses), low magnetization (from cold work and welding etc.) as well as lower cost of fabrication (machining, extrusion, etc.). Compact non-evaporable getter (NEG) pumps are used due to the space constraints. As in situ beampipe bakeout is practically impossible, a program was carried out to measure aluminum alloy outgassing rates at various controlled processing (bakeout, purified dry nitrogen venting, etc.). As a measure of vacuum system cost reduction, metal knife-edge seal flanges made of non-coated aluminum alloy (type 6013-T6) were developed as the beam diagnostics ports. The results of the outgassing study were used to validate vacuum pumping system design via 3D simulation. In this presentation, we report the status of CBETA vacuum system design and fabrication. Measurements of aluminum alloy outgassing rate and tests of aluminum knife-edge flanges will also be discussed.

9:00am **VT-TuM4 Vacuum System for CHESS-U Upgrade at CESR**, ***Xianghong Liu***, *S. Barret, D.C. Burke, J.V. Conway, A.T. Holic, Y. Li, A. Lyndaker*, Cornell Laboratory for Accelerator-Based Sciences and Education

A sextant of Cornell Electron Storage Ring (CESR) will be upgraded with Double Bend Achromat (DBA) lattice and CHESS Compact Undulators (CCUs) to significantly boost the performance of Cornell High Energy Synchrotron Source (CHESS). A lot of efforts are being made in preparation for the final installation in late 2018 for this upgrade project, dubbed CHESS-U. With this upgrade, CESR will be converted from a counter-propagating two-beam ring to a single-beam ring. The beam energy will be increased from 5.3 GeV to 6 GeV, and the beam current for normal operation will be increased from 120 mA to 200 mA. Because of the geometrical constraints from the magnets, the beampipe aperture of this new section is 52mm (horizontal) by 22mm (vertical), which is much smaller than the rest of CESR. The vacuum pumping for this new section will be different too, consisting of a combination of Non-Evaporable Getter (NEG) strips, modular NEG pumps, and ion pumps.

The beam pipes are mainly made of three types of aluminum extrusions, fitting inside quadrupole magnets, dipole magnets, and undulators respectively. All extrusions have cooling water channels to handle the thermal load from synchrotron radiation. The same channels are also used for vacuum hot-water bake-out. Dipole extrusions are formed to the correct bending radius by stretch forming in a softer temper, and heat treated to higher temper after forming. With required space available, the dipole extrusion includes an ante-chamber for NEG strip (SAES St 707) pumping. The NEG strip is activated by resistive heating to about 400°C for half an hour. The electrically insulating support mechanism of the NEG strip is adapted from the design used in APS. Instead of being built from extrusions, the dipole chamber where the X-ray beam exits is made of two machined halves that are welded together; a cylindrical crotch is inserted at the flared end of this chamber to absorb approximately 4 kW of synchrotron radiation.

In this presentation, we will give an overview of the design of the vacuum system, and report the estimated pressure profile based on Molflow$^+$ calculations, some design details of major components, results from NEG strip pumping tests, and progress in vacuum chamber productions.

9:20am **VT-TuM5 Newly Designed Alumina Ceramics Beam Pipe with Large Aperture for RCS in J-PARC**, ***Junichiro Kamiya***, *M. Kinsho*, Japan Atomic Energy Agency, *K. Abe*, HIPSD, Japan

The 3 GeV Rapid Cycling Synchrotron (RCS) in J-PARC aims to generate one of the highest power protons in the world. The design extraction beam power is 1 MW, which consists of $8.3 \times 10^{13}$ protons per bunch with 3 GeV energy at 25 Hz repetition rate. The rapid change of the magnetic field at such repetition rate causes the induced current if the beam pipe was made of metal. Therefore, beam pipes of alumina ceramics were used. The cross-sectional diameters of the pipes range from 250 to 500 mm, as is the case for the titanium beam pipes and bellows. There are several cross-sectional shapes corresponding to the various beam shapes. The beam pipes in the dipole and quadrupole/sextupole magnets have racetrack and circular shapes, respectively. The beam pipes in injection magnets have racetrack and rectangular shapes. Unique cross-sectional shape is adopted for the ceramics beam pipes for the injection quadrupole magnet. Because the injection beam and circulating beam pass through the injection quadrupole magnet, its cross-section has a racket shape fitting into 500 mm diameter. Recently this ceramics pipes for the injection quadrupole magnets were newly designed. In the new design, the bellows are attached to the titanium sleeve of the beam pipe by welding to obtain the better maintainability in the narrow area under high radioactivation level. In the conference, we will report the design concept of the new alumina ceramics beam pipes with unique shape and the several results of the verification tests.

9:40am **VT-TuM6 Vacuum Performance of Taiwan Photon Source Storage Ring**, ***Hsin-Pai Hsueh***, *G.Y. Hsiung, J.R. Chen*, National Synchrotron Radiation Research Center, Taiwan, Republic of China

The Taiwan Photon Source storage ring vacuum system has been developed to be pre-baked and installed under vacuum for 14-m arc sections. The straight sections were in-situ baked followed the installation of adjacent arc sections. During first stage commissioning, foreign object was found and the bending vacuum chamber of this particular arc section was replaced without baking (neither pre-baked and installed under vacuum, nor in-situ baking). Subsequently, four more bending chambers in other four different arc sections were replaced without baking either. Since this time saving method is different from our system design philosophy, a detailed pressure and mass spectrum analysis is necessary. From measured data, the photon stimulated desorption is no longer as dominant as we would like it to be as designed. The thermal outgassing is more than 25% of total outgassing at highest current (400mA or above). The total beam dose is almost 1500 Amp-hour. The photon-stimulated-desorption (PSD) pressure over beam current ($\Delta P/I$) is 2.33E-11 Pa/mA. In this presentation, the analysis results will be presented.

11:00am **VT-TuM10 The Vacuum System Design of a New FEL Test Facility (CLARA) at STFC Daresbury Laboratory**, ***Keith Middleman***, STFC, UK

Recent UK government funding has facilitated the construction of Phase 1 of a unique FEL accelerator test facility (CLARA – Compact Linear Accelerator for Reserach Applications). This test facility will allow the UK to reserach a variety of FEL operating modes to establish a roadmap for the UK and its plan to build a UK FEL user facility.

This paper will look specifically at the vacuum system design of this unique accelerator detailing the challenging design of the photoinjector, the FEL section and the possible use of NEG coating and the requirement for implementing a differential pumping scheme to separate two vacuum systems with 3 orders of magnitude pressure difference over 50 cm. Many other aspects of the accelerator design will be described and data showing the ’real’ perfromance of the accelerator presented.

11:20am **VT-TuM11 EBL2: Realization and Qualification of an EUV Exposure System**, ***Michel van Putten***, *N.B. Koster, A.F. Deutz, B.A.H. Nijland, P.J. Kerkhof, P.M. Muilwijk, B.W. Oostdijck, J. Westerhout, C.L. Hollemans, E. te Sligte, W.F.W. Mulckhuyse, F.T. Molkenboer, A.M. Hoogstrate, P. van der Walle, J.R.H. Diesveld, A. Abutan*, TNO, Netherlands

In 2014, TNO started the design of a new facility to test samples with EUV light (13.5 nm). This facility is called EUV Beam Line 2 (EBL2) and enables study of the interaction of lithographic photomasks, optics and other samples with EUV light by irradiation, *real-time* imaging ellipsometry and *in vacuo* XPS surface analysis.

The integration of EBL2 started in Q2 of 2016 and at the end of 2016 the major milestone – *first light* – was reached. Currently, the building phase of EBL2 being completed. During Q3 of 2017 we anticipate to complete the qualification. Once qualified, the EBL2 facility will be accessible for external customers and research groups.

The realization of such a facility is the translation from a design to a manufactured, integrated and tested system. During AVS63 the realization of some of the modules was presented, this presentation will discuss the integration of the complete system. Challenges in this are: motion in vacuum, use of UHV compatible materials, alignment of EUV optics.

The qualification of the EBL2 facility was done in three steps: module verification, system verification, and system validation. During the verification steps, EBL2 and its constituent modules were assessed against specifications. Next was system validation where the ability to satisfy user needs was verified.

This presentation will focus on the completion of the realization of EBL2 and results of the system verification and validation phases.

EBL2’s EUV irradiation performance is discussed in terms of EUV power, vacuum cleanliness, positioning of samples like reticles, and the setup and control of the sample environment in terms of positioning, temperature and gas environment.

11:40am **VT-TuM12 Construction and Commissioning of Tri Alpha Energy C2W machine**, ***Alan Van Drie***, Tri Alpha Energy

Tri Alpha Energy (TAE) is researching a novel fusion concept of energetic ions magnetically trapped as large orbits in a Field Reverse Configuration plasma (FRC). TAE has completed building and commissioning its latest machine, C2W.

The talk will first give a brief overview to TAE’s concepts and C2W, followed by a discussion of the physics that drive the vacuum requirements, such as divertor gas loads and how we solved many of the technical vacuum challenges in order to meet our performance goals. Specifically, C2W has four 15m$^3$ divertors where $H_2$ neutral particles from the plasma are pumped at a rate of 2,000 m$^3$/s. This large pumping is achieved through chemisorption onto titanium films deposited onto LN2 cooled multi-scaled surfaces. Additionally, each divertor has a 200m$^3$/s activated charcoal cryopump optimized for pumping $H_2$.

# Tuesday Afternoon, October 31, 2017

## Exhibitor Technology Spotlight Workshops
## Room: West Hall - Session EW-TuL

## Exhibitor Technology Spotlight
**Moderator:** Chris Moffitt, Kratos Analytical, Inc.

12:40pm **EW-TuL2 Design and Application of a New Laboratory-Based Scanning XPS/HAXPES Instrument**, *R. Inoue, H. Yamazui, K. Watanabe*, ULVAC-PHI, Japan, *S.R. Bryan*, ***John Newman***, *J.E. Mann*, Physical Electronics

X-ray Photoelectron Spectroscopy (XPS) is a widely used surface analysis technique with many well established industrial and research applications. The surface sensitivity (top 5-10 nm) of XPS and its ability to provide short-range chemical bonding information make the technique extremely popular in materials characterization and failure analysis laboratories. While its surface sensitivity is an important attribute, in some cases, the depth of analysis of XPS is not sufficient to analyze buried interfaces without first sputter etching the sample surface. However, sputter etching can often lead to alterations of the true surface chemistry. For this reason, some scientists turn to another technique - Hard X-ray Photoelectron Spectroscopy (HAXPES), available in some synchrotron radiation facilities. HAXPES utilizes X-rays typically defined as having energies greater than 5 keV. Depending on the energy used, these hard x-rays can provide for depths of analysis 3 or more times those of soft x-rays used on conventional XPS systems. This presentation will describe a newly developed laboratory-based instrument, the PHI Quantes, equipped with monochromated scanning Al Kα (1486.6 eV) and Cr Kα (5414.9 eV) x-ray sources, thus enabling both traditional XPS and HAXPES experiments in the same instrument. Combining both soft and hard x-ray analyses, we can gain an even better understanding of composition with depth and information at buried interfaces.

1:00pm **EW-TuL3 Application of X-ray Photoelectron Spectroscopy for the Characterisation of Biomaterials**, *C. Moffitt*, Kratos Analytical Ltd, *D. Surman*, Kratos Analytical Limited, *S.J. Coultas*, ***Jonathan Counsell***, Kratos Analytical Limited, UK

The Kratos AXIS series of photoelectron spectrometers are now widely applied to the characterisation of surfaces of biological interest. With its high energy resolution and excellent sensitivity at selected areas, XPS is routinely used to determine the surface chemistry of materials which interact with the native-tissue, organ or function in a body. Both the AXIS Supra and AXIS Nova utilize large sample holders and, when combined with the standard automated sample transfer capability, provides the ability for high sample throughput. These strengths are demonstrated in the XPS characterisation of printed micro-patterned co-polymer arrays leading to the discovery of novel biopolymers. The high spatial resolution imaging capability of the AXIS spectrometers is also used to probe the lateral distribution of surface chemistry of these co-polymer array samples. The recent development of the gas cluster ion source (GCIS) for depth profiling 'soft' materials means that XPS is no longer limited to simple surface analysis. The characterisation of the sub-surface and bulk biomaterial properties is now a reality and is demonstrated in the depth profiling of drug eluting bioresorbable stents. The efficacy of these stents is dependent on the drug distribution through the coating which is measured during a GCIS depth profile. In this presentation we will demonstrate the capabilities of the latest Kratos X-ray photoelectron spectrometers lateral resolution, depth distribution of elemental and chemical states, and detection sensitivity through the characterisation of biomaterials.

1:20pm **EW-TuL4 Advanced Photoelectron Spectroscopies Setup As a Key for Current Research**, ***Lukasz Walczak***, PREVAC, Poland

PREVAC is intended to provide advance equipment for professionals around the world to state-of-the-art research and development in the field of nanoscience and nanotechnology. We would like to promote the latest products, equipment, technology solutions and innovations for the photoelectron spectroscopies field. Few selected PES systems will be presented for study of important topics, including new materials, topological insulators, surface alloys, superconductors and others phenomena. Details technical descriptions from the systems and subsystems will presented for the laboratory and synchrotron research. Also, it will be displayed some new development of the cry manipulators and various types of the photoelectron spectroscopy components.

1:40pm **EW-TuL5 Advanced Ion Beam Techniques for Thin Films and Structuring**, ***Marcel Demmler***, AARD

Latest techniques using Ion Beam Technology for localized trimming of thin films to Angstrom level, CMP error correction, precision angled sidewalls, and highly adjustable selectivity of etch.

2:00pm **EW-TuL6 From Surface Spectrometry to 3D Analysis - Latest Trends and Instrumentation for TOF-SIMS**, ***Nathan Havercroft***, ION-TOF USA, *R. Moellers, A. Pirkl*, ION-TOF GmbH, Germany

During the last 25 years IONTOF has continuously made significant development efforts to further improve the instrumentation for Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and related techniques. Some of the most recent achievements include in-situ sample preparation and tomography by FIB, enhancement of maximum count rates and dynamic range in conventional depth profiling of inorganic materials, the design of a TOF-SIMS / SPM combination instrument, as well as the integration of an Orbitrap$^{TM}$ mass spectrometer with unrivalled mass resolution and mass accuracy into the TOF.SIMS 5 instrument. IONTOF's, new TOF.SIMS NCS instrument platform combines all the well-known options of our high-end TOF.SIMS 5 system with the possibility to perform in-situ SPM measurements. The sophisticated, large area SPM unit has a scan range of up to 80 x 80 µm$^2$ and is ideally suited to provide topographic information for SIMS measurements. Beside AFM, MFM, KPFM and multi-frequency modes it also supports a unique surface profiler mode which allows for fast measurements of large SIMS craters. The new piezo sample stage with submicron position accuracy ensures fast and precise movement between the TOF-SIMS and the SPM measurement position. Depth profiling of organic materials, e.g. layer systems for optical and electronic devices, can be ideally performed using gas cluster ion beams (GCIB) in combination with TOF-SIMS. For optimum performance, a dual-beam approach is usually utilized, employing a lower energetic quasi DC sputter beam for material removal and a short-pulse small-spot analysis beam for optimal mass spectral and imaging performance. However, molecular identification of unknown substances, e.g. contaminants, is usually hampered by constraints in mass resolution and mass accuracy of the TOF analyzer. Furthermore, ions generated in the sputter phase of the dual-beam experiment are lost for analysis. In order to overcome these limitations, a TOF / OrbitrapTM SIMS hybrid instrument has been developed in order to combine all advantages of a state-of-the-art TOF-SIMS with the mass spectrometry performance of a Q Exactive$^{TM}$ HF mass analyzer. The Q ExactiveTM HF provides a mass resolution of more than 240,000 @ m = 200 u, <1 ppm mass accuracy, and full MS/MS capabilities for structural analysis of complex molecules. By utilizing these unique features, the SIMS analyst can make peak identifications with much greater confidence.

## 2D Materials Focus Topic
## Room: 16 - Session 2D+BI+MN+SS-TuA

### Surface Chemistry, Functionalization, Bio and Sensor Applications
### Moderator: Matthias Batzill, University of South Florida

2:20pm **2D+BI+MN+SS-TuA1 Preserving Chemically Modified Graphene from Thermal and Chemical Loss of Functionality**, ***Keith Whitener***, *W.-K. Lee*, Naval Research Laboratory, *R. Stine*, NOVA Research, *J.T. Robinson, D. Kidwell, C. Tamanaha, P.E. Sheehan*, Naval Research Laboratory

Chemical functionalization can dramatically alter graphene's properties, enabling one to tune its chemical and physical properties for a wide range of applications. To be useful, these modifications must be stable; however, some of these chemical modifications can be unstable, allowing the material to partially revert to unfunctionalized graphene over time. In this talk, we present our detailed studies of the kinetics of graphene hydrogenation and dehydrogenation. Single layer hydrogenated graphene can be dehydrogenated via thermal, mechanical, and chemical routes. Interestingly, bilayer graphene is much more robust to both chemical and thermal dehydrogenation than is single layer graphene. Possible mechanisms for this difference in reactivity will be discussed. Finally, we leverage the insights from these studies to first fabricate functional chemistries and electronic devices on graphene and then to transfer the devices *in toto* onto arbitrary substrates including biological ones. This enables graphene to act like a chemical "sticky note", transferring chemical and physical properties from one surface to another.

2:40pm **2D+BI+MN+SS-TuA2 Chemical Vapor Sensing with 1T/2H Phase Engineered MoX$_2$ Films**, ***Adam Friedman***, *A.T. Hanbicki, F.K. Perkins, G.G. Jernigan, J.C. Culbertson, P.M. Campbell*, Naval Research Laboratory

Transition metal dichalcogenides (TMDs) show remarkable potential for use in chemical vapor sensor devices. They are inexpensive, inherently flexible, low-power, can be grown in large areas, and have shown high sensitivity and selectivity to electron donor analyte molecules. However, for most devices the conductance response is dominated by Schottky contacts, to the detriment of the sensitivity and obscuring the intrinsic sensing capability of the devices. We use contact engineering to transition the contacts in a MoS$_2$ FET-based chemical vapor sensor to the 1T conducting phase, leaving the channel in the 2H semiconducting state, thus providing functional Ohmic contacts to the device. We show that the resultant sensors have greatly improved electrical characteristics, are more selective, and recover fully after chemical vapor exposure—all major improvements to previous MoS$_2$ sensor devices. We study the dynamics of the sensing reactions identifying two possible models for the chemical sensing reaction with physisorption likely dominant. Additionally, we present both conductance and optical evidence that the phase transition can be induced in MoX$_2$ films by a saturating dose of strong electron donor vapor. We find that the conductance response to strong electron donors in both monolayer MoS$_2$ and MoSe$_2$ FET devices ceases after moderate exposure, with final value of the conductance being on order of that expected for the 1T phase. We also examine chemically exposed TMD films intermittently interrogated with Raman and photoluminescence spectroscopy. We observe the appearance of weak characteristic 1T phase Raman features for MoS$_2$ and we observed a quenching of the photoluminescence of both TMD films that is recoverable with annealing. The data cannot by explained solely by doping mechanisms. Our results suggest a mechanism for a new type of passive chemical vapor sensor.

[1] F.K. Perkins, A.L. Friedman, et al., *Nano Lett*. **13**, 668-673 (2013).

[2] A.L. Friedman, F.K. Perkins, et al., *Sol. St. Elec*. **101**, 2-7 (2014).

[3] A.L. Friedman, F.K. Perkins, et al., *Nanoscale***8**, 11445 (2016).

3:00pm **2D+BI+MN+SS-TuA3 Nanopores in 2D Materials**, ***Aleksandra Radenovic***, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

Atomically thin nanopore membranes are considered to be a promising approach to achieve single base resolution with the ultimate aim of rapid and cheap DNA sequencing. Recently, we made advances in using nanopore platform for its integration with 2 D materials such as graphene or MoS2. Translocation of various types of DNA exhibits a signal amplitude that is five times higher than in the case of solid-state Si3N4 membranes and a SNR of more than 10. These features are highly desirable for event detection and we take advantage of them by showing the electric-field induced unfolding of a 48 kbp long DNA molecule within the nanopore which manifests itself in the quantization of the current drop. Although single nucleotide identification and DNA sequencing using biological pores have already been demonstrated their fragility, difficulties related to measuring pA-range ionic currents together with their dependence on biochemical reagents, make solid state nanopores an attractive alternative. In this talk I will address novel applications that address identification of single nucleotides but as well go beyond DNA sequencing. We use novel solid state nanopore platform based on atomically thin nanopore membranes in 2D materials such as graphene or molybdenum disulfide for DNA detection, sequencing, water desalination and osmotic power generation.

4:20pm **2D+BI+MN+SS-TuA7 Spectroscopic Observation of Oxygen Dissociation on Nitrogen-Doped Graphene**, ***Mattia Scardamaglia***, University of Mons, Belgium, *T. Susi*, University of Vienna, Austria, *C. Struzzi*, Unviersity of Mons, Belgium, *R. Snyders*, University of Mons, Belgium, *G. Di Santo, L. Petaccia*, Elettra-Sincrotrone Trieste, Italy, *C. Bittencourt*, University of Mons, Belgium

The reactivity of carbon nanomaterials towards oxygen is very poor, limiting their potential applications as low-cost, high-yield catalysts. However, nitrogen doping is an established way to introduce active sites that facilitate interaction with gases [1,2]. This boosts the materials' reactivity for gas/bio sensing and enhances their catalytic activity for the oxygen reduction reaction, promising to substitute expensive metals in fuel cell cathodes. Despite this interest, the role of differently bonded nitrogen dopants in the interaction with molecular oxygen is obscured by experimental challenges and has so far resisted clear conclusions. We study the interaction of molecular oxygen with graphene doped via nitro-gen plasma by in situ high-resolution synchrotron techniques, supported by density functional theory core level simulations [3,4]. The interaction with oxygen gas leads to the dissociation of the molecule and the formation of carbon-oxygen single bonds on the graphene surface, along with a band gap opening and a rounding of the Dirac cone. The change of the N 1s core level signal indicates that graphitic nitrogen is responsible for the observed mechanism: it catalyses the dissociation of an absorbed oxygen molecule, after which the two O atoms chemisorb with epoxy bonds to the nearest and next-nearest carbon neighbours of the graphitic nitrogen. Our findings help resolve existing controversies and offer compelling new evidence of the ORR pathway.

1. Liu, X., Dai, L. (2016) Carbon-Based Metal-Free Catalysts. Nat. Rev. Mater., 1, 16064.
2. Ni, S., Li, Z., Yang, J. (2012) Oxygen Molecule Dissociation on Carbon Nanostructures with Different Types of Nitrogen Doping. Nanoscale, 4, 1184-1189.
3. Scardamaglia, M. et al., (2016) Tuning Nitrogen Species to Control the Charge Carrier Concentration in Highly Doped Graphene. 2D Mater., 3, 11001.
4. Scardamaglia, M. et al., (2017) Spectroscopic observation of oxygen dissociation on nitrogen-doped graphene. Submitted

4:40pm **2D+BI+MN+SS-TuA8 Back to Black: Can Molecular Networks Preserve the Surface of Black Phosphorus?**, ***Vladimir Korolkov***, The University of Nottingham, UK, *I.G. Timokhin, R. Haubrichs*, CristalTech Sàrl, Switzerland, *S. Yang, M. Schröder*, University of Manchester, UK, *P.H. Beton*, The University of Nottingham, UK

Black phosphorus (BP), one of several allotropic forms of phosphorus, has a layered structure and is a narrow gap semiconductor with a bulk band gap of ~0.3 eV. Similar to other layered materials it can be exfoliated with scotch tape to form a single layer of black phosphorus known as phosphorene. Unlike gapless graphene, phosphorene has a band-gap which was predicted, and later confirmed to be ~2 eV. The band gap is thickness dependent and thus can be easily tuned. Since the first reports of exfoliation of BP, and some 100 years after the first high-pressure synthesis of black phosphorus crystals by Bridgman in 1914, phosphorene or few layered BP has been widely used to construct transistors, including flexible devices.

One of the biggest challenges in BP and phosphorene research remains its stability under atmospheric conditions.

In this work we explore a new route to the solution of this problem through an investigation of the compatibility of BP with the formation of supramolecular networks which have monolayer thickness and are stabilised by non-covalent in-plane interactions, specifically hydrogen bonding. We find that supramolecular networks can be formed on BP and demonstrate this for a mono-component nanoporous array of trimesic acid (TMA) and the bimolecular network formed by cyanuric acid (CA) and melamine (M). While the more open TMA array does not passivate the BP surface, the hexagonal melamine cyanurate (CA.M) array is highly effective and provides protection under ambient conditions over a period of more than three months. In addition, we identify the orientation of the CA.M relative to the rows of phosphorus atoms at the surface and, normal to the rows, observe moiré effects which are characteristic of a well-ordered interfacial structure. We have further demonstrated that CA.M monolayers on BP provide a stable platform for the sequential growth of additional molecular layers, for example, 1,2,4,5-tetrakis(4-carboxyphenyl)benzene (TCPB), leading to the formation of a supramolecular heterostructure and demonstrating the facility for further functionalisation of the BP substrate.

Our work demonstrates that a single layer of CA.M can successfully passivate the surface of BP and preserve it intact for at least 3 months. We believe that this facile approach of depositing a passivating organic monolayer stabilised by in-plane non-covalent bonding could be extended to the protection of other two-dimensional materials with air sensitive atomically flat surfaces, and is likely compatible with other solvents and molecules.

The work also presents outstanding examples of high resolution AFM imaging achieved under ambient conditions.

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5:00pm **2D+BI+MN+SS-TuA9 Defect-mediated Properties of Single-layer MoSe$_2$**, ***Sara Barja***, Materials Physics Center, San Sebastián, Spain, *S. Wickenburg, Z.-F. Liu, Y. Zhang,* Molecular Foundry, Lawrence Berkeley Lab, *A. Pulkin*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *S. Refaely-Abramson, B. Schuler,* Molecular Foundry, Lawrence Berkeley Lab, *H. Ryu,* Lawrence Berkeley National Laboratory, *D. Qiu,* University of California at Berkeley, *M. M. Ugeda,* CIC nanoGUNE, Spain, *Z.-X. Shen,* Stanford Institute of Materials and Energy Sciences, *S.-K. Mo, M.B. Salmeron,* Lawrence Berkeley National Laboratory, *M.F. Crommie*, University of California at Berkeley, *D.F. Ogletree*, Molecular Foundry, Lawrence Berkeley Lab, *O.V. Yazyev*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *J.B. Neaton, A. Weber-Bargioni*, Molecular Foundry, Lawrence Berkeley Lab **INVITED**

Properties of two-dimensional transition metal dichalcogenides are highly sensitive to the presence of defects in the crystal structure. A detailed understanding of the defect electronic structure may lead not only to the control of the material's properties through defect engineering towards a particular device application, but also may lead the emergence of novel physico-chemical functionalities. We show how linear mirror twin boundaries and individual atomic defects in single-layer MoSe$_2$ alter the electronic structure of the pristine semiconductor. Such linear and point defects tend to be highly localized in the plane, which imposes the need of experimental and theoretical characterization of the defects at the atomic level. Using non-contact atomic force microscopy and scanning tunneling spectroscopy, we directly correlate the morphology and electronic properties of structural defects in MoSe$_2$ at the defect-length scale. We provide direct evidence for the existence of isolated, one-dimensional charge density waves at mirror twin boundaries in single-layer MoSe$_2$. We also determine the local density of states of Se vacancies in monolayer MoSe$_2$ and discuss the correlation to density functional theory calculations, studying the role of the GW approximation to reproduce the energetics of the valence and conduction band as measured in the experimental dI/dV spectra.

5:40pm **2D+BI+MN+SS-TuA11 Scalable Flexible Graphene Gate TMD Biosensors**, ***RamSurya Gona***, *C.H. Naylor, A.T. Johnson*, University of Pennsylvania

Two dimensional transition metal dichalcogenides, such as MoS$_2$ and WS$_2$, have been shown to be promising materials for use in bio-sensing. I will present our work on the fabrication of scalable flexible MoS$_2$ field effect transistors with patterned graphene back-gate. Flexible devices were fabricated on a Kapton substrate and incorporating graphene as the back-gate material due to its biocompatibility and its favorable physical properties. Monolayer MoS$_2$ single-crystal flakes were grown over large area by chemical vapor deposition, and then transferred onto a pre-patterned electrode array, resulting in a device yield > 70% and an average mobility of 1.0 cm$^2$V$^{-1}$s$^{-1}$. To create nano-biosensors, the surface of the MoS$_2$ was functionalized via a reengineered mu-opioid receptor and the devices were tested against opioid solutions of various concentrations. This work provides a pathway for the integration of MoS$_2$ and other TMDs onto flexible/wearable/implantable devices that for trace detection of opioids or other chemicals. This work was supported by the National Science Foundation through EFRI 2DARE ENG-1542879

6:00pm **2D+BI+MN+SS-TuA12 Development and Validation of Polarized Models for Peptide-Graphene Interactions**, ***Amanda Garley***, University of Colorado Boulder, *N. Saikia*, Michigan Technological University, *R. Berry*, Air Force Research Laboratory, *H. Heinz*, University of Colorado Boulder

Biosensor technologies require the understanding of interactions between organic and inorganic materials to tune electric response functions, such as peptide assembly on graphitic substrates. Laboratory characterization of specific interactions and molecular assembly can be complemented by atomistic molecular simulations, as well as by quantum-mechanical analysis of band gaps and expected conductivity.

As a first step, we improved common dispersive interatomic potentials for graphite to include pi electron density at virtual sites. The new model reproduces experimental cation-pi energy, X-ray structure, density, cleavage energy, hydration energy, contact angle and elastic constants. As a result we have improved existing models which gave the wrong sign of hydration energies and deviations up to 1000% in these properties from experiment. The parameters are embedded in CHARMM, CVFF, TEAM-AMBER, and other common force fields as part of the INTERFACE force field. An analysis of binding residues, binding energies, conformations, and dynamic information of molecular mobility on the surfaces will be presented.

## 2D Materials Focus Topic
## Room: 15 - Session 2D-TuA

## Growth of 2D Materials
### **Moderator:** Taisuke Ohta, Sandia National Laboratories, Center for Integrated Nanotechnologies

2:20pm **2D-TuA1 A New Approach to the Synthesis of High-quality Graphene on Silicon Carbide**, ***Piotr Ciochoń***, *J.J. Kołodziej*, Institute of Physics, Jagiellonian University, Poland

**A new approach to the synthesis of high-quality graphene on silicon carbide**

One of the most widely used methods of graphene synthesis is the graphitization of the (0001) and (000-1) surfaces of silicon carbide crystal. In order to obtain high quality graphene, it is necessary to slow down the excessive sublimation of silicon, observed at temperatures at which graphene ordering occurs. The most widely used method to accomplish this is carrying out the graphitization process in the presence of atmospheric pressure of inert buffer gases, such as argon.

We propose an alternative approach to solve this issue, which relies on exposing SiC surface during thermal annealing to the high-purity beam of silicon, obtained from an external sublimation source. The proposed solution has two advantages over the buffer-gas method. Firstly, it reduces the amount of impurities present near the surface by several orders of magnitude, as compared to even the purest inert gases at the atmospheric pressure. Secondly, it allows for precise control over the process parameters, leading to the possibility of near-equilibrium graphitization.

We have performed a thorough study of the process, systematically varying the parameters, such as graphitization temperature, process time and the silicon flux density and found that the synthesized graphene is characterized by very high degree of crystallographic ordering, low concentration of defects and large size of monocrystalline domains. Varying the process parameters, we were have been able to control the number of synthesized graphene layers, without the deterioration of overall graphene quality. Moreover, the process has shown a remarkable reproducibility, allowing for proper standardization of the synthesized material, a step considered crucial for the widespread introduction and use of graphene-based devices.

Our method allows for fast, reproducible synthesis of a very high-quality graphene directly on an insulating surface and is perfectly suited for preparing hybrid heterostructures and intercalation of foreign atoms. We have performed preliminary studies of intercalation with Cr atoms, during the graphitization process, as our approach allows to overcome several problems, resulting in unsuccessful past attempts.

2:40pm **2D-TuA2 Cation-Eutectic Transition via Sublattice Melting in CuInP$_2$S$_6$/In$_{4/3}$P$_2$S$_6$ van der Waals Layered Crystals**, *M.A. Susner,* Air Force Research Laboratory, *M. Chyasnavichyus, Q. He, B.S. Conner, D.A. Cullen, P. Ganesh, D. Shin, J.W. McMurray, A. Borisevich, M.A. McGuire,* Oak Ridge National Laboratory, *Y. Ren,* Argonne National Laboratory, ***Petro Maksymovych***, Oak Ridge National Laboratory

Metal thiophosphate materials family offers a materials toolbox with broad functionality that includes magnetism, ferrielectricity and electron correlations. Here we report on heterostructure engineering of layered ferrielectric CuInP$_2$S$_6$, which controllably introduces 1D and 2D chemical boundaries into the crystal on bulk scale. Single crystals of mixed Cu$_{1-x}$In$_{1+x/3}$P$_2$S$_6$ spontaneously phase separate into ferrielectric (CuInP$_2$S$_6$) and paraelectric (In$_{4/3}$P$_2$S$_6$) chemical domains, providing a new route to functional in-plane heterostructures in layered and 2D materials. We used high temperature x-ray diffraction and in-situ electron microscopy to conclusively demonstrate that this material forms a single phase at high temperature, and to identify the mechanism by which the phase separation proceeds upon cooling. Above 500 K $Cu_{1-x}In_{1+x/3}P_2S_6$ adopts a heavily disordered structure with respect to metal/vacant sites occupying the octahedral sites within a layer, thus indicating high $Cu^+$ and $In^{3+}$ mobilities. However, the framework of $P_2S_6$ anions remains invariant across this transition. Considering the results of our detailed measurements of the transition temperature as a function of Cu/In ratio, we propose that this transition can be understood as eutectic melting on the cation sublattice, conceptually similar to intermediate temperature behavior of halide superionic conductors. Such a model suggests that the transition temperature for the melting process is relatively low because it requires only a partial reorganization of the crystal lattice. As a result, varying the cooling rate through the phase transition controls the lateral extent of chemical domains over several decades in size, forming an intricate mesh of in-layer heterostructures comprised of domains with distinct cation compositions. Heterostructures can be formed, destroyed, and reformed by thermal cycling. Using this mode of lattice manipulation, we demonstrate that the ferroelectric $T_c$ can be both increased to a nearly record level (about 20K higher than the pure bulk $CuInP_2S_6$ of 305K) and completely suppressed well below room temperature, without changing the physical sample, chemical composition, or loss of reversibility. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy.

[1] Susner et al., "Metal Thio- and Selenophosphates as Multi-Functional van der Waals Layered Materials", Advanced Materials, in press (2017)

[2] Susner et al., Cation-eutectic transition via sublattice melting in $CuInP_2S_6/In_{4/3}P_2S_6$ van der Waals layered crystals, ACS Nano in review (2017).

3:00pm **2D-TuA3 Direct, Real-Time Observation of Layer-by-Layer Growth of a 2D Semiconductor using *In Situ* X-ray Synchrotron Radiation**, *H.J. Bullen, R.K. Nahm, S. Vishwanath, G. Xing,* ***James Engstrom***, Cornell University

Two-dimensional materials, in particular transition metal dichalcogenides, are attracting considerable interest from both fundamental and applied viewpoints. In a number of studies, thin films of these materials are produced by techniques such as exfoliation. While these techniques have been invaluable concerning the measurement of electronic and other important physical properties, growth of thin films of these materials is essential to fully exploit their promise in a variety of devices. In particular, there is a great need to develop an understanding of the growth process such that one can at will deposit an arbitrary number of layers (e.g., 1, 2, 3 etc.) on a variety of possible substrates. Here we report on the metal-organic MBE growth of thin films of $WSe_2$ on sapphire substrates using $W(CO)_6$ and elemental Se, where we monitor the process *in situ* and in real time with X-ray synchrotron radiation. In this work, we have two independent means to introduce the thin film constituents: a (supersonic) gas-source of $W(CO)_6$ in a carrier gas of He, and an effusion cell containing elemental Se. We can collect both the scattered X-rays, and those emitted due to fluorescence, both *in situ* and in real time. We have examined growth for a variety of conditions, including the flux and incident kinetic energy of the $W(CO)_6$, and the substrate temperature. After a short incubation time, we observe steady-state epitaxial growth of crystalline $WSe_2$ thin films. X-ray fluorescence confirms formation of a stoichiometric thin film of $WSe_2$. Perhaps most interestingly, during epitaxial growth we observe strong and sustained oscillations at the "anti-Bragg" condition for X-ray scattering, consistent with layer-by-layer growth. These results enable a direct determination of how each successive layer forms[1], and how these depend on process conditions. Concerning process conditions, we observe a spectacular change in the growth as the incident kinetic energy of the $W(CO)_6$ is varied. At sufficiently low values of the incident kinetic energy we observe no growth, while at higher values we observed sustained 2D LbL growth. These results point to the importance of incident kinetic energy in driving the dissociative chemisorption of the $W(CO)_6$ precursor.

[1] See, e.g., A. R. Woll, T. V. Desai and J. R. Engstrom, *Quantitative modeling of in situ x-ray reflectivity during organic molecule thin film growth*, Phys. Rev. B **84**, 075479/1-14 (2011).

3:20pm **2D-TuA4 Crystallization Kinetics of Photonically Annealed 2D Materials**, *N.R. Glavin, R.A. Vila, R. Kim, R.S. Rao, M.E. McConney, B. Maruyama, L.J. Bissell,* Air Force Research Laboratory, *R.H. Rai,* Air Force Research Laboratory; University of Dayton, ***Christopher Muratore***, University of Dayton

Synthesis of flexible electronic devices using low-cost, naturally abundant materials (e.g., $MoS_2$) directly onto inexpensive polymeric materials promises manufacturing of flexible 2D devices at economically viable scales enabling use of their unique physics in grand challenge areas of energy, healthcare, and national security. Recently-proven approaches for low temperature 2D synthesis suitable for flexible substrates developed by the authors include growth of amorphous materials with subsequent photonic annealing to access crystalline domain sizes up to several microns. This approach has been demonstrated for synthesis of large area ultrathin monolithic layers as well as $MoS_2/WS_2$/BN multilayers with pristine interfaces, allowing interrogation of intrinsic properties of 2D materials and their heterostructures as they apply to diverse optoelectronic devices. Detailed kinetic studies of crystal formation were accomplished through high throughput in-situ Raman spectroscopy at different surface temperatures and ambient conditions. With this technique, heterostructures were formed incorporating multiple TMD layers that were annealed simultaneously, and insights into the role of surface diffusion for metal and chacogen speices, and factors dictating activation energy for two-dimensional crystallization will be discussed.

4:20pm **2D-TuA7 Intercalation Then Ordering of Oxygen Leading to Isolation Then Etching of Monolayer *h*-BN on Copper**, *C. Ma, J. Park,* Oak Ridge National Laboratory, *L. Liu,* University of Tennessee, *Y.-S. Kim, M. Yoon,* ***Arthur Baddorf***, Oak Ridge National Laboratory, *G. Gu,* University of Tennessee, *A.-P. Li*, Oak Ridge National Laboratory

The interaction of *h*-BN, the thinnest 2D insulating material, with oxygen is important technologically, but has proven complex. *h*-BN has strong covalent bonds that exhibit great stability and multilayers have been recommended as an oxidation resistant barrier for both metal and graphene substrates. At the same time, oxygen is predicted to form adsorbed chains and then to cut *h*-BN sheets along the chains. We have exposed monolayer *h*-BN on copper substrates to air and then examined the surface with scanning tunneling microcopy (STM) and x-ray photoelectron spectroscopy (XPS) after annealing to 600°C in ultrahigh vacuum. The active adsorbent is identified as oxygen, as expected. More surprising is evidence that oxygen is intercalated between the *h*-BN and copper and forms both quasi-1D and 2D ordered patterns on the predominantly (100) oriented substrate. STM images display double rows of O in hollow sites forming quasi-1D chains preferably along the moiré patterns and, in areas of higher coverage nucleated by steps, a p(2×2)-O superstructure. Efficient O diffusion along moiré channels is supported by first-principles density functional theory (DFT). Despite searches, a p(2×2)O structure on clean Cu(100) has not been observed; instead, higher density c(2×2)O islands are created there. XPS intensities here are consistent with the lower coverage p(2×2)O stabilized by the *h*-BN layer. Intercalated O increases the *h*-BN to Cu distance thereby decreasing the van der Waals interaction. Both STM dI/dV and DFT reflect this increased isolation by a 1.7 eV increase in the monolayer band gap, governed by a decrease in the contribution of the Cu surface to the density of states.

Intercalated oxygen is ultimately not stable and extended annealing at 600°C etches away the *h*-BN. In contrast to previous models, *h*-BN is removed by oxygen found underneath rather than adsorbed on the surface. Etching occurs along *h*-BN zig-zag edges and leads to finally to complete removal of the film. These new mechanisms observed for oxygen introduction, organization, and etching offer opportunities to better understand the stability of *h*-BN monolayers and to exploit the addition of oxygen to modify electronic properties or for formation of nanoscale structures.

This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

4:40pm **2D-TuA8 Polished Nickel Substrates for Large-area Multilayer Graphene Films**, ***Stefan Lehnardt***, *J.T. Rowley, K. Larsen,* Brigham Young University, *J. Abbott,* Moxtek, *R.R. Vanfleet, R.F. Davis*, Brigham Young University

We show that the roughness of polycrystalline nickel has a significant effect upon the homogeneity of large-area multilayer graphene films grown via chemical vapor deposition. Nickel foil serves as a substrate/catalyst for this multilayer graphene growth. By mechanical polishing nickel foils and reducing roughness from ~100 nm to ~10 nm, we have obtained graphene films with fewer defects and greater thickness uniformity. Mechanical properties were determined by bulge testing and bending measurements on microscale cantilevers. Films from polished foils are thinner and show higher burst pressures.

5:00pm **2D-TuA9 Heterostructures of Carbon Nanomembranes and Graphene as a Platform for Electrochemical Sensing**, *D. Kaiser, A. Winter, C. Neumann,* Friedrich Schiller University Jena, Germany, *A. Centeno, A. Zurutuza,* Graphenea, Spain, *T. Weimann,* Physikalisch-Technische Bundesanstalt, Germany, ***Andrey Turchanin***, Friedrich Schiller University Jena, Germany

Chemical functionalization of single-layer graphene (SLG) is of key importance for applications in functional electronic devices such as, e.g., field-effect transistor (FET) based nanosensors. However, the electronic structure of graphene is typically degraded after the functionalization, which significantly restricts the applications. Here, we employ a route to non-destructive chemical functionalization of graphene with amino terminated 1 nm thick carbon nanomembranes[1] ($NH_2$-CNM) generated via electron beam induced crosslinking of aromatic self-assembled monolayers. The electrical response of the $NH_2$-CNM/SLG heterostructures in electrolyte-gated FETs shows their high electrical capacitance enabling for effective sensor applications. The electrochemical performance of CNM/graphene FETs for detection of pH-values was studied in parallel with their in detail surface science characterization. We show that the high electronic performance of pristine SLG is preserved in the developed amino-terminated hybrids and demonstrate the pH-sensing with excellent sensitivity and reproducibility. Finally, we discuss the perspectives for highly selective biological sensing with the developed device concepts.

[1] A. Turchanin and A. Gölzhäuser, Carbon Nanomembranes, *Adv. Mater.* 28 (2016) 5075

5:20pm **2D-TuA10 Nucleation of 2D $WS_2$ by Plasma Enhanced Atomic Layer Deposition from $WF_6$, $H_2$ Plasma and $H_2S$ – Impact on Grain Size and Charge Transport**, ***Benjamin Groven***, *A. Nalin Mehta,* University of Leuven, Belgium, *Q. Smets, T. Schram, H. Bender, W. Vandervorst, I. Radu, M. Caymax, M. Heyns, A. Delabie,* IMEC, Belgium

To exploit the semiconductor properties of two-dimensional (2D) transition metal dichalcogenides in ultra-scaled nano-electronic devices across large area substrates, these materials need to be deposited with a highly crystalline structure and a controlled number of monolayers by manufacturable deposition techniques. Where the majority of the 2D materials in literature are grown by Chemical Vapor deposition (CVD), Atomic Layer Deposition (ALD) is investigated here as an alternative deposition technique. In ALD, (sub-)monolayer growth control is possible as the deposition is based on self-limiting surface reactions. In addition, due to the relatively low deposition temperature, the 2D materials can be grown directly on temperature sensistive structures at Back-End-Of-Line (BEOL) compatible deposition temperatures. As such, a material transfer from the growth to the target substrate can be avoided.

In Atomic Layer Deposition (ALD), the structure of 2D materials is determined by the nucleation mechanisms. However, the nucleation mechanisms of 2D materials by ALD have so far not yet been investigated. In this work, we investigate the nucleation behavior of $WS_2$ from a recently reported Plasma-Enhanced (PE)ALD process from $WF_6$, $H_2S$ and $H_2$ plasma [1]. We show how the crystallinity and domain size of these layers depends on the starting substrate and the deposition temperature, and how they influence the semiconductor properties of $WS_2$. $WS_2$ is grown on 300 mm Si substrates covered with either 30 nm amorphous $Al_2O_3$ or 90 nm thermally grown $SiO_2$.

At 300 °C, the growth of $WS_2$ is strongly enhanced on the $Al_2O_3$ surface. The high nucleation density of $(2.2\pm0.1) \cdot 10^{14}$ /cm$^2$ promotes fast closure of the first $WS_2$ layer. On the other hand, the combination of the high nucleation density with lateral and vertical growth contributions limits the crystal domain size to 5-30 nm. By choosing a substrate that has a lower reactivity towards the PEALD precursors, e.g. $SiO_2$, the nucleation density decreases to $(2.0\pm0.1)\cdot10^{11}$ /cm$^2$. An even lower nucleation density of $(6\pm1) \cdot10^{10}$ /cm$^2$ is obtained on $SiO_2$ by increasing the deposition temperature to 450 °C due to the increasing mobility of the ad-atoms on the surface. By lowering the reactivity of the $H_2$ plasma to further delay nucleation, the $WS_2$ crystals grow primarily in a lateral direction, which further increases the crystal grain size to 250 nm. Despite the low deposition temperatures, the $WS_2$ behaves as a semiconductor in back-gated transistors, that show an $I_{max}/I_{min}$ ratio of at least $10^5$ [2].

[1] B. Groven et al., *Chem. Mater.*, 2017, 29 (7), pp 2927–2938

[2] T. Schram, Q. Smets et al. VLSI satellite workshop 2017 (accepted)

5:40pm **2D-TuA11 *Surface* Intercalation of Two Disparate Metals in Graphite: Copper and Dysprosium**, ***Ann Lii-Rosales****, *P.A. Thiel,* Iowa State University and Ames Laboratory

In this study, we use STM to investigate the intercalation of atomic metals, copper (Cu) and dysprosium (Dy), in the *surface* of graphite that is pre-treated with $Ar^+$ bombardment.

*Surface* intercalated Dy rafts have a characteristic height of 0.61 ± 0.03 nm, with structured moiré patterns atop faceted rafts. DFT calculations on intercalated Dy rafts support our experimental observation: instead of a *dilute*, $(\sqrt{3}\times\sqrt{3})R30°$ arrangement of Dy atoms as in the well-known stage-1 Dy graphite intercalation compound (GIC), our Dy rafts are *dense* and are composed of three contiguous layers of Dy sandwiched between graphitic layers.

In the case of Cu, for which no *bulk* GIC's are known, we achieve *surface* intercalation of Cu in ion-bombarded graphite. Spanning temperatures of 600 – 900 K, the morphology of intercalated Cu responds sensitively. At 600 – 800 K, intercalated Cu forms faceted islands that are variable in heights, ranging from 1.7 nm to as tall as 35 nm. At 850 K, intercalated Cu no longer forms faceted islands; instead, round clusters ranging from ~0.3 nm to 10 nm tall are present. At 900 K, small and round features ~0.3 nm tall prevail. Larger clusters are presumably removed by desorption. High resolution imaging atop a Cu island sheds light on the number of carbon overlayers and shifting in the stacking sequence of carbon lattice, potentially due to strain as a result of intercalation.

Relative to known *bulk* GIC's, our work shows that metals on graphite *surfaces* adopt configurations that are different in two ways. First, the metals form dense intercalated surface islands; and second, metals which do not intercalate in the bulk can do so on the surface. *Surface* intercalation of other metals can be envisioned.

This work is supported by the US Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division through the Ames Laboratory, which is operated by Iowa State University under contract # DE-AC02-07CH11358.

## 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.

References: Gendron, F. et al., 'Puzzling lack of temperature dependence of the PuO2 magnetic susceptibility explained according to ab-intio wavefunction calculations', J. Phys. Chem. Lett. 2017, 8, 673-678. 'Ligand NMR chemical shift calculations for paramagnetic metal complexes: 5f1 vs. 5f2 actinides', J. Chem. Theory Comput. 2016, 12, 5309-5321. 'Magnetic properties and electronic structure of neptunyl(VI) complexes: Wavefunctions, orbitals, and crystal-field models', Chem. Eur. J. 2014, 20, 7994-8011. Knecht, S. et al, 'A nonorthogonal state-interaction approach for matrix product state wave functions', J. Chem. Theory Comput. 2016, 12, 5881-5894. Silver, M. et al., 'Characterization of berkelium(III) dipicolinate and borate compounds in solution and the solid state', Science 2016, 353, aaf3762.

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]

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* **NSTD Student Award Finalist**

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].

1. U. D. Wdowik, P. Piekarz, D. Legut, and G. Jaglo, Phys. Rev. B **94**, 054303 (2016).

2. P. Maldonado, L. Paolasini, P. M. Oppeneer, T. R. Forrest, A. Prodi, N. Magnani, A. Bosak, G. H. Lander, and R. Caciuffo,

Phys. Rev. B 93, 144301 (2016).

3. Y. Yun, D. Legut and P. M. Oppeneer, J. Nucl. Mat. **426**, 109 (2012).

4. K. Parlinski, Z.-Q. Li, and Y. Kawazoe, Phys. Rev. Lett. **78**, 4063 (1997); K. Parlinski, Software PHONON, ver. 6.15, Krakow, Poland, (2015).

## Applied Surface Science Division
## Room: 13 - Session AS+TF-TuA

## Problem Solving Using Surface Analysis in the Industrial Laboratory

**Moderators:** Jeffrey Fenton, Medtronic, Paul Vlasak, The Dow Chemical Company

2:20pm **AS+TF-TuA1 TOF-SIMS MS/MS for Industrial Problem Solving**, *G.L. Fisher, D.M. Carr,* Physical Electronics, *T. Miyayama, S. Iida,* ULVAC-PHI, Japan, ***Scott Bryan***, Physical Electronics

One of the most common requests in an industrial analytical lab is to distinguish between “good” and “bad” samples of supposedly the same composition. For failure analysis labs, the goal is often to determine the source of contamination or defects in a production process with poor yield. Identifying contamination left behind from different cleaning procedures or after extended use is also a common request. In all these circumstances, one does not know ahead of time what chemical compounds are present. TOF-SIMS is an ideal technique for these applications because it has high sensitivity, high specificity, and parallel detection of all masses. One complication is that real-world samples usually have a complex mixture of compounds on the surface, making the TOF-SIMS spectrum difficult to interpret. Further, the use of a wide variety of different primary ion beams (e.g. $Ga^+$, $In^+$, $Au^+$, $Bi^+$, $C_{60}^+$, and $Ar_n^+$) has complicated the use of TOF-SIMS spectral databases for compound identification due to large changes in relative peak intensities from one beam to another.

A MS/MS capability was recently integrated into a TOF-SIMS instrument to make compound identification easier [1,2]. It allows unambiguous identification of both organic and inorganic peaks above *m/z* 200, where the mass accuracy is insufficient to identify the composition of a peak by its exact mass. A MS/MS spectrum from a single precursor mass is much easier to match using a spectral database compared to using the original complex TOF-SIMS spectrum. In addition, the MS/MS spectrum of a given precursor ion is independent of the primary ion used to generated it.

Several case studies will be given where MS/MS was needed to identify compounds from an analysis of industrial samples. Two modes of MS/MS will be compared and contrasted. One is based on collision induced dissociation (CID) with inert gas and the other is based on post source decay (PSD).

[1] G.L. Fisher, J.S. Hammond, P.E. Larson, S.R. Bryan, R.M.A. Heeren, J. Vac. Sci. Technol. B 34(3), 2016, 03H126-1.

[2] G.L. Fisher, A.L. Bruinen, N. Ogrinc Potočnik, J.S. Hammond, S.R. Bryan, P.E. Larson, R.M.A. Heeren, Anal. Chem., 88, 2016, 6433-6440.

2:40pm **AS+TF-TuA2 *In Situ* Molecular Imaging of Switchable Ionic Liquids**, ***Juan Yao***, *D. Lao, X.F. Yu, S. Nune, D. Heldebrant, Z.H. Zhu, X.Y. Yu*, Pacific Northwest National Laboratory

Switchable ionic liquids (SWILs) are emerging green solvents in industry for cleaner separation and efficient biomass production, for instance. However, the liquid structure and composition of SWILs are not fully understood. Besides some off-line analyses using NMR and IR, our knowledge of the SWIL is quite limited. We used in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study SWILs in this work. SWILs are introduced into a vacuum compatible microfluidic channel for analysis by liquid SIMS. Two model systems have been investigated. The first consists of 1, 8-diazabicycloundec-7-ene (DBU) and 1-hexanol with different $CO_2$ loadings. The second is primarily made of koechanol with various $CO_2$ loadings. Koechanol acts as both acid and base in the latter. Our results show two coexisting liquid phases in the two SWIL systems. This phenomenon was only hypothesized in previous theory prediction. We are able to provide the first physical evidence of the complex liquid-liquid interface using three-dimensional chemical mapping with submicrometer resolution. In addition, more complex stoichiometry is discovered as a result of SWIL formation. More importantly, we provide the first chemical spatial mapping elucidating the evolved liquid-liquid interface as a result of SWIL formation. We anticipate the more detailed molecular level understanding of the liquid structure and composition are instrumental to build the foundation for predicative material synthesis and more versatile industrial applications.

3:00pm **AS+TF-TuA3 Employing a Surface and Bulk Analytical Approach for the Synthesis and Characterization of Ophthalmic Biomaterials**, ***Daniel Hook***, *A. Hoteling, W. Nichols, I. Nuñez, K. Wygladacz*, Bausch + Lomb, Inc. **INVITED**

**Background:**

During the development of a new soft contact lens material three areas of focus; regulatory requirements, manufacturing requirements and customer needs, are often used to guide the overall activities of the material development process.

Regulatory requirements are associated with material properties that are collected using methods defined by standards organizations and accepted by regulatory bodies globally. While this data is mandatory for the registration and approval of a contact lens material it is incomplete in that it only defines the basics of the material.

Manufacturing requirements such as speed of polymerization and completeness of reaction provide critical information so that an effective material can be made in a cost effective manner.

Finally, patients will demand a material that can be worn comfortably while correcting vision over the course of the wearing schedule. Patient focused parameters such as incorporation of wetting agents that create a wettable surface as well as a robust surface that will withstand handling of the course of several weeks of wear area also critical to success.

**Methods:**

The ISO methods 18369-4:2006, 4.6, 18369-4:2006, 4.4, 18369-4:2006, 4.5 were used to collect bulk properties of water content, oxygen permeability and refractive index while ANSI method Z80.20.2010, 7.10 was used to collect captive bubble contact angle data (CBCA). Photo-Differential Scanning Calorimetry (Photo DSC), Gas Chromatography-Mass Spectrometry (GC-MS) and Liquid Chromatography - Mass Spectrometry (LC-MS) were used to measure polymerization kinetics and monomer consumption. X-ray Photoelectron Spectroscopy (XPS) data was collected to understand surface uniformity and product consistency while Atomic Force Microscopy (AFM) was used to assess surface morphology over the course of the wearing schedule.

**Results and Conclusion:**

Data summarizing the submission for samfilcon A, a 46% water, 114 Dk material will be presented. CBCA coupled with XPS data will demonstrate a consistent surface wettability and chemistry across multiple lens powers and lens lots. Photo DSC, GC-MS and LC-MS will illustrate how the lens polymerizes in two distinct time resolved phases enabling the incorporation of polyvinyl pyrrolidone wetting agent into the lens bulk and surface. Together the analytical data will provide a unique picture of the data set needed for regulatory approval along with satisfying the manufacturing requirements and patient needs for a successful ophthalmic biomaterial.

4:20pm **AS+TF-TuA7 Surface Properties and Interfacial Bonding of Anodic Aluminium Oxides and Organic Resins**, ***Shoshan Abrahami***, *T. Hauffman*, Vrije Universiteit Brussel (VUB), Belgium, *De KoK*, Fokker Aerostructures BV, Papendrecht, The Netherlands, *Gudla, Ambat*, Technical University of Denmark (DTU), Denmark, *J.M.C. Mol*, TU Delft, Netherlands, *H. Terryn*, Vrije Universiteit Brussel, Belgium

Aluminium pretreatment for bonding purposes needs to produce a stable oxide with optimal chemical and structural characteristics for adhesion with the organic resin. Contributions at the interface region can be related to adsorptive interactions as well as mechanical interlocking between the two phases. To separate between these two effects, we applied either barrier-type or porous-type oxides on two sets of specimens. This paper presents an overview of a study on the relation between oxide properties and interfacial bonding, as affected by the nature of electrolyte and the anodizing conditions, as well as changes in the chemistry of the organic resin (epoxy, phenol, silanes). A detailed characterization of different anodic oxides and its effect on the adsorption of resin-derived functional molecules was performed using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). Results indicate significant changes in the chemical composition of the oxides as a function of the electrolyte[1]. Mechanical peel test performance indicate that the initial bond strength is independent of the oxide surface chemistry, while the stability under the ingress of water is correlated to the amount of surface hydroxyls[2]. The presence of phosphates and sulphates did not alter bonding mechanisms, only the availability of hydroxyls. Further, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to characterize the geometrical modifications to the pore- and oxide structure in porous-type oxides. In addition, energy-dispersive X-ray spectroscopy (EDS) profiles were acquired on TEM cross-sections to assess the oxide structure and concentration of resin inside the pores. Linking these morphological features to peel results show that two types of modifications are crucial for the formation of a strong and durable bonding[3]. A minimum pore size is needed for the resin to fill the oxide pores for good initial adhesion. Surface roughness, on the other hand, was found beneficial for the durability of the bond upon the ingress of water. Overall, the results demonstrate that both surface chemistry and oxide morphology contribute to the strength and durability of an adhesive bond.

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2. Abrahami, S. T., et al., Effect of Anodic Aluminum Oxide Chemistry on Adhesive Bonding of Epoxy. J. Phys. Chem. C 2016, 120, 19670-19677.

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4:40pm **AS+TF-TuA8 Practical Considerations of Different Ion Sources for Industrial Applications: The Good, the Bad, and the Indifferent**, ***William Stickle***, *C.N. Young, M.D. Johnson*, HP Inc., *B. Schmidt*, Physical Electronics USA

In recent years advances in ion gun technology have resulted in the routine application of cluster ion sources for analyses in industrial R&D labs. Most industrial laboratories study a wide variety of material systems ranging from polymers to inorganic thin films; many of these material systems require analysis not just of the as received surface, but also of and through the depth of a thin film. The purpose of this talk is to compare and contrast the benefits and drawbacks of performing routine XPS analyses using a mono atomic argon ion source compared with a $C_{60}^+$ ion source and an argon gas cluster ion source. From a practical standpoint, i t is important to understand the sputter induced chemistry that may be created by these various sources and the trade-offs for applying these different primary ion sources for routine surface chemical analyses. The effects of preferential sputtering and chemical changes or reactions of metal oxides will be discussed. Several different material systems are examined and discussed by comparing the information obtained using mono atomic argon, an argon gas cluster source and a $C_{60}^+$ ion source for enhancing and clarifying 'routine' analyses. The different types of samples to be discussed will include polymers, fluoropolymer systems, amorphous metals and their oxides and multilayer thin films.

5:00pm **AS+TF-TuA9 Surface Analysis in an Industrial Setting: Non-ideal Real World Samples**, ***Vincent Smentkowski***, General Electric Global Research Center **INVITED**

The top few nanometers of a sample is defined as the surface. The surface is where most chemical reactions take place. There are many instances where the surface of materials are designed/functionalized in order to optimize properties and improve device performance; there are other instances where the surface becomes compromised and the material/device performance degrades following treatment and/or use. Accurate characterization is essential in order to understand material/device performance.

Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS), Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Scanning Probe Microscopy (SPM) are the most common, and commercially available, surface analysis techniques. These techniques provide complimentary information regarding both the composition and microstructure of the surface of a sample and often compliments bulk analysis.

In my talk, I will discuss the characterization challenges faced in an industrial setting where the surface analyst is often provided non-ideal samples and is asked to provide both a rapid and complete analysis of the sample. The criticality of talking with the person that submits the sample to understand their issue(s) and what they expect from the analysis (as well as being certain they realize possible complications) will be highlighted via real samples. I will also show a few examples where proof of principle results provided interesting data, however the data were not scientifically meaningful.

5:40pm **AS+TF-TuA11 C 1s Peak of Adventitious Carbon Aligns to the Vacuum Level: Dire Consequences for Material's Bonding Assignment by Photoelectron Spectroscopy**, ***Grzegorz Greczynski***, *L. Hultman*, Linköping University, Sweden

X-ray photoelectron spectroscopy (XPS) is an irreplaceable analytical tool in materials research providing information about surface chemistry and composition. The unambiguous bonding assignment relies, however, on the correct measurement of binding energy (BE) values, which is often a nontrivial task due to the lack of an internal BE reference. C 1s signal from ubiquitous carbon contamination on samples forming during air exposure, so called adventitious carbon (AdC) layers, is the most common BE reference in XPS studies. Our literature review shows that in 58% of the top-cited papers dealing with XPS studies of magnetron sputtered films published between 2010 and 2016 in peer-reviewed journals, C 1s of AdC was used as a BE reference, while, alarmingly, the remaining papers lack information about any referencing method used. Within the first group, C 1s peak was set quite arbitrary at the BE varying from 284.0 to 285.2 eV. This serious inconsistency contradicts the very notion of a BE reference, which per definition should be connected with one single-energy value.

In this work, we examine the reliability of using AdC for XPS BE referencing by measuring the position of C 1s peak for a series of transition metal (TM) nitride thin film layers that exhibit a well-defined Fermi edge cut-off serving as an internal BE reference. Measurements are performed as a function of the AdC layer thickness, which scales with the air exposure time. We show that the BE of C 1s peak $E^F_B$ varies by as much as 1.44 eV, depending on the underlying (TM)N.[i] This is a factor of ten more than the typical resolvable difference between two chemical states of the same element, *which makes BE referencing against the C 1s peak unreliable and thus inadvisable for the purpose*. Surprisingly and reassuringly, we find that C 1s shifts correlate to changes in sample work function $\Phi_{SA}$, such that the sum $E^F_B+\Phi_{SA}$ is constant at 289.50±0.15 eV, irrespective of materials system and air exposure time, indicating vacuum level alignment. This discovery allows for significantly better accuracy of chemical state determination through a complementary measurement of $\Phi_{SA}$ and referencing to C 1s set at $289.50-\Phi_{SA}$, which as we demonstrate, yields consistent results for the whole series of TM nitrides, irrespective of air exposure time. Our findings are not specific to nitrides and likely apply to all systems where charge transfer at the AdC/substrate interface is negligible.

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[i] G. Greczynski and L. Hultman, *ChemPhysChem* 18 (2017) 1507

6:00pm **AS+TF-TuA12 Band Energy Alignment Studies at Heterojunction by X-ray Photoelectron Spectroscopy (XPS)**, ***Jisheng Pan***, Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), Singapore

The performance of any type of hetero-junction device is determined by two kinds of interface parameters: the band discontinuities and the built-in potential. Therefore, determining heterojunction band offsets and tuning them to a desired application would have an obvious impact on the optimization of the devices. Many techniques have been developed to determine the interfaces and to understand the microscopic origin of the interface properties. XPS is more widely used technique to study band alignment of heterojunction, probably due to its capability to simultaneously detect interface chemical and electronic properties which can be exploited for fully understanding of distinct correlations between the thin film material characteristics and device performance. There are two ways to obtain energy band offsets using XPS. One is direct measurement of valence band spectrum from interface, and this spectrum is simply considered as a superposition of substrate-related and overlayer-related valence band spectra. A nonlinear least squares fit is performed to separate it to substrate-related and overlayer-related valence band spectra to determine two valence band maxima and, valence band offset (VBO) of interface. The conduction-band offset CBO is deduced from VBO and suitable reference gap values of two materials at interface. It can be seen that the accuracy of the band offsets determined through this way depends on the fitting procedure. In order to overcome the above problem and obtain reliable band offset data, a method was proposed to determinate band offsets by combination of core level and valence band spectra. No fitting procedure is involved in this method. However, accurate XPS determination of band alignment in this way requires careful consideration of many other possible effects. In this paper, we have studied the effects of chemical shift, differential charging, band bending and photoemission final state on the determination of heterojunction band offsets using Kraut's method. The method has also been applied to determinate energy-band alignments of molybdenum disulphide ($MoS_2$) monolayer on high-k dielectric oxides such as $Al_2O_3$ and $ZrO_2$. The VBO at monolayer $MoS_2/Al_2O_3$ ($ZrO_2$) interface was measured to be 3.31 eV (2.76 eV), while the CBO was 3.56 eV (1.22 eV). For bulk $MoS_2/Al_2O_3$ interface, both VBO and CBO increase by 0.3 eV, due to the upwards shift of Mo 4dz$^2$ band. The symmetric change of VBO and CBO implies Fermi level pinning by interfacial states. Our finding ensures the practical application of both p-type and n-type $MoS_2$ based complementary metal-oxide semiconductor and other transistor devices using $Al_2O_3$ and $ZrO_2$ as gate materials.

## 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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(2) M. Tsurkan, K. Chwalek, S. Prokoph, A. Zieris, K. Levental, U. Freudenberg, C. Werner (2013) Adv Mater 25:2606

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(5) K. Chwalek, M.V. Tsurkan, U. Freudenberg, C. Werner (2014) Sci Rep 4:4414

(6) L.J. Bray, M. Binner, A. Holzheu, J. Friedrichs, U. Freudenberg, D.W. Hutmacher, C. Werner (2015) Biomaterials 53:609

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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.

## Electronic Materials and Photonics Division
## Room: 14 - Session EM+SS-TuA

### Surface and Interface Challenges in Semiconductor Materials and Devices
**Moderator:** Anthony Muscat, University of Arizona

2:20pm **EM+SS-TuA1 Selective Atomic Layer Deposition of MoSi$_x$ on Si (001) in Preference to Silicon Nitride and Silicon Oxide**, ***JongYoun Choi***, *C.F. Ahles,* University of California, San Diego, *R. Hung, N. Kim,* Applied Materials, Inc., *A.C. Kummel*, University of California, San Diego

As MOSFETs size shrinks to <10 nm in a three dimensional structure (FinFET), electrical losses at the contacts must be minimized. Consequently, selective atomic layer deposition (ALD) of transition metal disilicides are of great interest due to their ability to minimize parasitic resistance and avoid lithograph onto a three dimensional structure. Selective ALD of metallic tungsten (W) via a fluorosilane elimination process have been demonstrated using $WF_6$ and $SiH_4$ or $Si_2H_6$.[1,2] This selectivity was achieved by an inherently favorable reactivity of the precursors on hydrogen-terminated Si versus OH-terminated $SiO_2$. In this W deposition process, $SiH_4$ was used as a reducing agent for W while the reactions byproducts was $SiF_4$. Here, we demonstrated that sub-stoichiometric silicide, $MoSi_x$ (x=0.4 – 1.1), can also be selectively deposited on H-terminated Si (001) in preference to SiOx and SiN using $MoF_6$ and $Si_2H_6$. X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical composition of $MoSi_x$ ateach experimental step. It was observed that Si-H terminated silicon allowed single cycle nucleation of $MoSi_x$ at the substrate temperature of 100-120°C in contrast to an inherent chemical passivation (non-reactivity) on $SiO_x$ and SiN surfaces. To enable formation near stoichiometric $MoSi_x$, excess amount of $Si_2H_6$ was dosed after 5 ALD cycles to incorporate more Si into the $MoSi_x$ film while maintaining selectivity since the $SiO_x$ was unreactive to even high doses of $Si_2H_6$. This substrate-dependent selectivity was retained up to 5 - 10 ALD cycles. By applying a mixture gas of ($H_2$+$MoF_6$) instead of $MoF_6$ dosing, (as previous shown by Kalanyan et al[2]), the inherent selectivity was greatly improved and the nucleation of $MoSi_x$ was impeded up to at least 20 ALD cycles on SiN without perturbing $MoSi_x$ deposition on silicon. The growth rate of $MoSi_x$ on Si was ~0.8 Å/cycle; therefore, even 10 selective ALD cycles is sufficient for deposition of contacts. To confirm an *in-situ* selective deposition as well as the thickness of the film, $MoSi_x$ was deposited on a sample patterned with Si and SiON and the cross-section of the patterned sample was quantified using transmission electron microscopy (TEM). The surface morphology and roughness were measured using *ex-situ* atomic force microscopy (AFM) and *in-situ* scanning tunneling microscopy (STM). $MoSi_x$ on Si was conformal and atomically flat surface with root mean square (RMS) of 2.8 Å. Post-annealing in a ultra-high vacuum at 500°C for 3 mins further decreased the RMS roughness to 1.7 Å.

1. Thin Solid Films, **241**, 374 (1994)
2. Chem. Mater., **28**, 117-126 (2016)

### 3:00pm **EM+SS-TuA3 Interface and Border Traps, their Passivation and the Reliability of Alumina Dielectric / Indium Gallium Arsenide Gate Stacks**

***Paul McIntyre***, Stanford University **INVITED**

Both interface defects and border traps - charge traps in the gate oxide - influence the behavior of InGaAs metal-oxide-semiconductor (MOS) devices. This presentation will summarize the different effects of interface and border traps on the temperature- and bias-stress behavior of aluminum oxide/InGaAs MOS gate stacks, and will describe methods for passivating these defects both prior to and after gate dielectric deposition. The influence of local interface chemistry and the complex role of hydrogen as a defect passivant are highlighted.

In one set of experiments, a temperature dependent border trap response for $Al_2O_3$ gate dielectrics is investigated. This behavior is unexpected for defects that have typically been reported to charge and discharge through direct tunneling of electrons from the n-type substrate. Temperature dependent border trap frequency dispersion of the accumulation capacitance and conductance is found to be correlated with the presence of a defective interfacial layer, which can be intentionally produced either by excessive exposure to hydrating or oxidizing species during atomic layer deposition of $Al_2O_3$ or by use of a previously-reported aqueous HCl clean of the InGaAs surface prior to ALD. These results point out the sensitivity of the temperature dependence of the border trap response in metal oxide/III-V MOS gate stacks to the presence of processing-induced interface oxide layers, which alter the dynamics of carrier trapping at defects that are not located at the semiconductor interface.

We also report on the effects of pre- and post-atomic layer deposition (ALD) defect passivation with hydrogen on the trap density and reliability of $Al_2O_3$/InGaAs gate stacks. Reliability is characterized by capacitance-voltage hysteresis measurements on samples prepared using different fabrication procedures and having different initial trap densities. Despite its beneficial ability to passivate both interface and border traps, a final forming gas ($H_2/N_2$) anneal (FGA) step is found to induce a significant hysteresis. This is caused by hydrogen depassivation of defects in the gate stack under bias stress, supported by the observed bias stress-induced increase of interface trap density, and strong hydrogen isotope effects on the measured hysteresis. Additional strategies, beyond hydrogen annealing, for more stable interface defect passivation on InGaAs will be discussed briefly.

### 4:20pm **EM+SS-TuA7 Controlling GaAs and Si Oxide Surface Energies**

***Karen L Kavanagh***, Simon Fraser University, Canada, *N. Herbots, A. Brimhall, R. Van Haren, Y.W. Pershad, S. Suhartono, E. Landeros, R.J. Culbertson,* Arizona State University, *R. Islam*, Cactus Materials

Bonding two different semiconductors into a single integrated device can yield economic, medical, and human benefits by increasing performance. Si and GaAs bonding can increase solar cell efficiency and, if the bonding is hermetic, the lifetime of bonded sensors and optoelectronic circuits is extended by reducing percolation. Bonding occurs when the electronic properties of the two surfaces complement each other, to enhance efficient electron transfer.[1] Complementary surfaces can be identified through measurement of their total surface energy, $\gamma^T$, since this property can be modeled by Van Oss theory, to consist of three component interaction energies: molecular dipoles (Lifschitz-Van der Waals), $\gamma^{LW}$, electron donors, $\gamma^-$, and electron acceptors, $\gamma^+$. Measurements of the total and individual components of the surface energy of Si and GaAs (100) surfaces has been carried out using contact angle measurements of liquid drops with known surface energies, ranging from polar (18 MW water), apolar (α-bromo-naphthalene) to non-polar (glycerin). Accurate reproducible results are obtained using class 100 clean-room environments and analysis of multiple drops of each type of surface energy. This three liquid contact angle analysis (3LCAA) brings a much greater level of sophistication to this well-known and apparently-simple method. When carried out with semiconductor-level control of cleanliness, the contribution of each component to the total surface energy of Si (100) native and non-native oxides has been found to depend linearly on $\gamma^{LW}$. In hydrophobic oxide surfaces, $\gamma^T$ is due almost entirely to molecular interactions, $\gamma^{LW}$, to within a few % error. Thus, the highly-passivated, thermally-grown $SiO_2$ surface with few defects or impurities, has a surface energy of 35.7 ± 3 $mJ/m^2$ that is entirely explained by $\gamma^{LW}$. However, $\gamma^T$ can be raised to 57.3 ± 2 $mJ/m^{2.}$ by generating defects, and unsaturated or dangling bonds that interact with electron acceptors and or donors. This situation applies to heavily-etched, oxide surfaces, or chemically-oxidized surfaces. The contributions from $\gamma^-$and $\gamma^+$, raises the total surface energy $\gamma^T$ up to 40% above that of $\gamma^{LW}$, which is found to remain nearly constant. Similar experiments with GaAs (100) surfaces as a function of surface preparation find that the Si-doped GaAs native oxide to be hydrophobic with a $\gamma^T$of 35 ± 3 $mJ/m^2$, with $\gamma^{LW}$contributing 98 ± 2%, thus close to the entirety of $\gamma^T$. This indicates a well-reacted native oxide. [1] *Herbots N. et al. US Patent 9,018,077 (2015); 9,589,801 (2017).*

### 4:40pm **EM+SS-TuA8 *In Situ* $Si_3N_4$ Surface Layer on GaN-on-Si Heterostructure for High Power Operation**

***Chien-Fong Lo***, *O. Laboutin, X. Gao, C.K. Kao, H. Marchand, W. Johnson, R. Pelzel*, IQE

Gallium nitride based devices have been delivering their promise of high power and high frequency operation as a capable replacement for silicon based devices, applications, owing to highly desirable III-nitride physical properties [1] . However, device performance is limited by excessive Schottky gate leakage, which results in high gate subthreshold leakage and leakage instability. These in turn cause high off-state drain leakage, a degradation of power efficiency, and ultimately device reliability problems.

Schottky leakage is caused by an excessive trap states density at the interface between the Schottky gate and the nitride semiconductor, resulting in excess negative charges on the barrier surface and/or in the barrier layer that induce current collapse in off-state operation. Dielectric capping of the III-nitride structure is one method to suppress the gate leakage in both forward and reverse bias, thereby mitigating current collapse and further improving the 3-terminal breakdown. Passivation with silicon nitride has been reported to reduce the current collapse and provide a relatively low state density at the $SiN_x$/III-N interface [2] and is widely used. However, in many instances, the $SiN_x$ passivation is done *ex-situ* from the GaN epi system which results in an oxide layer at the nitride/$SiN_x$ interface, which in turn reduces the efficacy of the passivation. Therefore, it is desirable to perform the $SiN_x$ deposition *in-situ* so that the semiconductor/$SiN_x$ interface is oxide-free.

*In-situ*, MOCVD $SiN_x$ films have been grown on 100–200 mm Si substrates and characterized with RBS, AFM, XRD/XRR, and *C-V* profiling. Stoichiometric silicon nitride films with good surface morphology and material properties have been achieved. Metal-insulator-semiconductor HEMT (MISHEMT) devices with *in-situ* $SiN_x$ capping layer were fabricated and compared with conventional GaN-capped HEMTs. Devices with *in-situ* passivation exhibit three orders of magnitude lower gate leakage current and improved 3-terminal breakdown (200V improvement at 10 µA/mm, see Fig. 1). Hall–Van der Pauw measurements performed on both GaN- and $SiN_x$-capped samples indicate that using *in-situ* $SiN_x$ results in a significant increase in channel carrier density, which is consistent with $SiN_x$ providing a reduced trap state density at the Schottky/semiconductor interface [3]. Additional electrical data including pulsed *I-V* will be presented to validate the improvements in switching performance. All of the nitride-based materials and $SiN_x$ passivation layers have been grown using a commercial MOCVD reactor ensuring cost-effective implementation for commercial power-switching applications.

### 5:00pm **EM+SS-TuA9 In-Vacuo Studies of Surface Structure and Surface Chemistry During Plasma-Assisted Atomic Layer Epitaxial Growth of InN Thin Films on GaN Substrates**

***Samantha Rosenberg***, ASEE (residing at NRL), *D.J. Pennachio,* University California Santa Barbara, *V.R. Anderson,* ASEE (residing at NRL), *N. Nepal,* U.S. Naval Research Laboratory, *C. Wagenbach,* Boston University, *A.C. Kozen,* ASEE (residing at NRL), *Z.R. Robinson,* SUNY Brockport, *J.A. Logan, S. Choi*, University California Santa Barbara, *J.K. Hite,* US Naval Research Laboratory, *K.F. Ludwig,* Boston University, *C.J. Palmstrøm,* University California Santa Barbara, *C.R. Eddy, Jr.*, U.S. Naval Research Laboratory

III-N semiconductors are well suited for applications in several important technological areas, including high current, normally-off power switches.[1-3] Such devices require heterostructures not readily achievable by conventional growth methods. While atomic layer deposition (ALD) is a versatile technique and has gained wide use, it does not offer the required level of crystallinity and purity for high-performance III-N semiconductor devices. Therefore, we have developed a technique adapted from ALD, called plasma-assisted atomic layer epitaxy (ALEp).[2]

Here we employ i*n-situ* and *in-vacuo* surface studies of GaN substrate preparation and InN ALEp growth to advance fundamental understanding of the ALEp process. We conduct *in-situ* grazing incidence small angle x-ray scattering (GISAXS) experiments at the Cornell High Energy Synchrotron Source, utilizing morphological evolution monitoring to investigate the growth interface during sample preparation at several different temperatures and film deposition at growth temperature. GISAXS information is complemented with *in-vacuo* x-ray photoelectron spectroscopy and reflection high-energy electron diffraction studies conducted at the Palmstrøm Lab at UCSB, where we consider traditional molecular beam gallium flash-off and atomic hydrogen etching as ways to produce the most suitable GaN surface for our ALEp-based approach.

1. N. Nepal, et al., Appl. Phys. Lett. 103, 082110 (2013)

2. C. R. Eddy, Jr, et al., J. Vac. Sci. Technol. A 31(5), 058501 (2013).

3. R. S. Pengelly, et al., IEEE Trans. Microwave Theory Tech. 60, 1764 (2012).

5:20pm **EM+SS-TuA10 Aqueous Ammonium Sulfide Treatments on SiGe Surfaces**, ***Stacy Heslop***, *L. Peckler*, *A.J. Muscat*, University of Arizona

Employing germanium (Ge) and/or silicon germanium (SiGe) as the active material in transistors has the potential to generate electronics that are faster and consume less power. The narrower band gaps and higher hole mobilities compared to silicon make these materials ideal candidates for the next generation of microelectronics, but their integration into current manufacturing is difficult due to the rapid oxidation of germanium. These oxides are unstable, electrically defective, and form a poor interface with the underlying substrate hindering their electrical performance. The native $GeO_2$ is water soluble and unable to protect the surface during liquid phase processing. To combat this, the oxidation is prevented by depositing a thin sulfide layer to chemically passivate the surface. Ammonium sulfide is a common passivation reagent due to the size and valency of the sulfur atom and its ease of integration into current industrial processes.

X-ray photoelectron spectroscopy (XPS) was used to study the effect of varying concentrations of aqueous ammonium sulfide on SiGe. No sulfide layer was detected for surfaces treated with aqueous ammonium sulfide and instead the surface reoxidized in solution. Hydrofluoric and hydrochloric acids were added to the ammonium sulfide solution to remove or prevent the formation of these oxides in solution. Samples treated with ammonium sulfide with added acid showed a sulfide layer. Increasing the concentration of HF and HCl increased the sulfur coverage but also increased the oxide coverage, suggesting the deposition of oxidized sulfur species.

Metal-insulator-semiconductor capacitors (MISCAPs) were fabricated for three different surface treatments. Capacitance –voltage and conductance data was used to quantify the density of interface defects ($D_{it}$). Samples treated with ammonium sulfide with added acid showed the highest sulfur coverage and had fewer interface defects ($1.4 \times 10^{12}$ $cm^{-2}$ $eV^{-1}$) compared to samples treated with aqueous ammonium sulfide or samples with no sulfur treatment.

6:00pm **EM+SS-TuA12 The Structural Stability and Phase Transition of $MoTe_2$ Activated by Thermal Annealing**, ***Hui Zhu***, *Q. Wang*, *C. Zhang*, *R. Addou*, *K.J. Cho*, *M. Kim*, *R.M. Wallace*, University of Texas at Dallas

Among group-VIB transitional-metal dichalcogenides (TMDs), semiconducting molybdenum ditelluride (2H-$MoTe_2$) with a similar bandgap to Si (~1.1 eV for monolayer and 1.0 eV for bulk state), is a promising candidate for electronic and photovoltaic applications.[1] Additionally, $MoTe_2$ possesses phase transition behavior, for example, the well-known phase transition between its semiconducting 2H structure and its semimetallic, distorted octahedral 1T' structure due to their small formation energy difference (~0.03 eV).[2] The thermally induced structural stability of $MoTe_2$ needs careful evaluation for nano-electronic device applications compared to the other TMDs due to a small electronegativity difference (~0.3) between Mo and Te, which may weaken the Mo-Te bonding strength. In this work, using scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and scanning transmission electron microscopy (STEM), we investigated the thermal structural stability of $MoTe_2$ heated under high vacuum conditions and discovered an interesting decomposition or phase transition process from 2H-$MoTe_2$ (initial) to 2H-$MoTe_2$ surface decomposition with random Te atomic vacancies (200 °C and 300 °C) to semi-periodic, "wagon wheel" patterns of 60° inversion domain boundaries ($MoTe_{1.5}$ at boundaries, 400 °C) to one dimensional, metallic $Mo_6Te_6$ nanowires (NWs, 450 °C).[3] Particularly, the $Mo_6Te_6$ nanowires registered along the <11-20> 2H-$MoTe_2$ crystallographic directions with lengths in the micrometer range. The metallic NWs can act as an efficient hole injection layer on top of 2H-$MoTe_2$ due to the favorable band-alignment. Furthermore, an atomically sharp $MoTe_2$/$Mo_6Te_6$ interface and van der Waals gap with the 2H layers are preserved. The work highlights an alternative pathway for forming new transition metal chalcogenide phases and will enable future exploration of their intrinsic transportation properties.

This research was supported in part by the **SWAN** Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, and the Center for Low Energy Systems Technology, one of the six SRC STARnet Centers, sponsored by MARCO and DARPA.

**Reference**

(1) Keum, D. H.; et. al. Bandgap Opening in Few-Layered Monoclinic $MoTe_2$. *Nat. Phys.***2015**, *11*, 482–486.

(2) Cho, S.; et. al. Phase Patterning for Ohmic Homojunction Contact in $MoTe_2$. *Science.***2015**, *349*, 625–628.

(3) Zhu, H.; et. al. New $Mo_6Te_6$ Sub-Nanometer-Diameter Nanowire Phase from 2H-$MoTe_2$. *Adv. Mater.***2017**, 1606264.

## Exhibitor Technology Spotlight Workshops
## Room: West Hall - Session EW-TuA

### Exhibitor Technology Spotlight Session
### Moderator: Chris Moffitt, Kratos Analytical, Inc.

4:00pm **EW-TuA6 eSpectra: Surface Science**, ***Jessica Hoy***, AIPP/AVS

When you search through scientific scholarly journals for specific information within the data, do you sometimes wish you didn't have to sort through multiple papers and the static figures buried within them but instead an organized set of graphs, datasets, or peak assignments? eSpectra: Surface Science is an online platform where you can access and plot peer-reviewed datasets of more than 4,000 spectra from 700 materials published in over 600 articles in Surface Science Spectra (SSS), the definitive international journal of spectral data published by the AVS. The only interactive tool of its kind, eSpectra includes XPS, AES, and UPS experimental techniques. Upload and plot your own data and compare it to SSS data to better understand, analyze, and validate your results. Download and print plotted graphs, or save, share, and store your graphs and data in a secure environment. We offer both free and Premium Access options. When you register for free, you also receive a 30-day free trial of Premium Access. Learn more today at eSpectra.aip.org.

## Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
## Room: 25 - Session HC+SS-TuA

### Advances in Theoretical Models and Simulations of Heterogeneously Catalyzed Reactions
### Moderator: Xiaofeng Feng, University of Central Florida

2:20pm **HC+SS-TuA1 Hindered Translator/Rotor Models for Calculating the Entropy of Adsorbed Species for Improved Micro Kinetic Models Based on Density Functional Theory Calculations**, ***Liney Arnadottir***, *L.H. Sprowl*, Oregon State University, *C. Campbell*, University of Washington **INVITED**

With the recent explosion in computational catalysis and related microkinetic modeling, the need for a fast, yet accurate, way to predict equilibrium and rate constants for surface reactions has become more important. Here a method to calculate partition functions and entropy of adsorbed species and equilibrium constants is presented. Instead of using the vibrational frequencies estimated from DFT and the harmonic oscillator approximation to calculate all modes of motion in the partition function, we use a hindered translator and hindered rotor model for the three modes of motion parallel to the surface, one for each of the two translations in the directions parallel to the surface and one for rotation about the axis perpendicular to the surface. This hindered translator and hindered rotor model joins the two limiting cases for adsorbates on a surface, the 2D ideal lattice gas (harmonic oscillator) model and the 2D ideal gas (free translator) model, making it valid over large temperature range. At the limit of low temperature, or high energy barrier, only vibrations are present and this model is the same as the harmonic oscillator approximation, while at high temperature, or low energy barrier, translations and rotations readily occur and this model becomes identical to the 2D ideal gas model for translations or the 1D free rotor model for rotations. The transition between the 2D ideal lattice gas (harmonic oscillator) model and the 2D ideal gas (free translator) model is surprisingly sharp, but modeled very closely by the hindered translator/rotor model. To verify this model, density functional theory was used to calculate adsorbate entropies of four different adsorbate species and found to agree well with experimental results.

3:00pm **HC+SS-TuA3 $CO_2$ Dynamics as a Product of Formate Decomposition on Cu(111)**, ***Fahdzi Muttaqien***, *H. Oshima*, *Y. Hamamoto*, *K. Inagaki*, *I. Hamada*, *Y. Morikawa*, Osaka University, Japan

Formate (HCOO) synthesis has been experimentally clarified to occur by the Eley-Rideal (ER) mechanism,[1] which suggests that the reaction rate depends on the initial energy of impinging $CO_2$. Since HCOO synthesis and decomposition are reversible reactions, the energy of impinging $CO_2$ must be related to the energy states of desorbed $CO_2$ from formate decomposition. Therefore, elucidation of HCOO decomposition dynamics is important to deduce optimal conditions for catalytic HCOO synthesis.

We performed ab initio molecular dynamics analysis to elucidate the dynamics of $CO_2$ from HCOO decomposition on Cu(111). We first investigated the translational energy of desorbed $CO_2$ from the velocity of center of mass of $CO_2$. The calculated translational energy (shown in Fig. 1 of Supp. Info) using PBE, PBE-D2, vdW-DF1, rev-vdW-DF2, and optB86b-vdW are 0.30 eV, 0.05 eV, 0.18 eV, 0.16 eV, and 0.11 eV, respectively. Those calculated $CO_2$ translational energy using PBE-D2 and vdW-DFs are in reasonable agreement with the experimental estimation (0.10 eV),[2] while PBE fails in predicting this energy.

We then explored the rotational and vibrational energies of $CO_2$ from HCOO decomposition. The rotational energy of $CO_2$ was calculated from its moment of inertia and angular momentum. We obtained that calculated $CO_2$ rotational energy varies between 0.08−0.11 eV. The $CO_2$ vibrational energies are evaluated based on the time evolution of the bond angle, C−O bond length, and difference between two C−O bond lengths of desorbed $CO_2$ (shown in Fig. 2 of Supp. Info). The vibrational energy of bending, symmetric stretching, and antisymmetric stretching modes are 0.25 eV, 0.11 eV, and 0.0015 eV, respectively. The vibrational energy of desorbed $CO_2$ bending mode is close to the third excitation energy of the vibrational energy of bending of isolated $CO_2$.

In summary, the vibrational energy of desorbed $CO_2$ bending mode is twice larger than the translational energy. Since HCOO synthesis from $CO_2$ and $H_2$, reverse reaction of the HCOO decomposition, is experimentally suggested to occur by the ER mechanism, our results indicate that the reaction rate of formate synthesis can be enhanced if the bending vibrational mode of $CO_2$ is excited rather than the translational, rotational, and/or stretching modes. These results are in contrast to the case of $CO_2$ dissociation, in which the $CO_2$ symmetric and antisymmetric stretching modes are more important to increase the dissociation rate.[3,4]

**References:**

H. Nakano *et. al.*, *J. Phys. Chem. B***105**, 1355 (2001).

J. Quan *et. al.*, *Angew. Chem. Int. Ed.* **56**, 3496 (2017).

T. Yamanaka, *Phys. Chem. Chem. Phys.***10**, 5429 (2008).

B. Jiang and H. Guo, *J. Chem. Phys.***144**, 091101 (2016).

### 4:20pm **HC+SS-TuA7 Reaction Mechanisms and Nature of Active Sites on Alloy Catalysts: Combining First-principles, Microkinetic Modeling, and Reaction Kinetics Experiments**

*Manos Mavrikakis*, University of Wisconsin - Madison **INVITED**

Using a combination of first-principles calculations, microkinetic modeling, and reactivity experiments, we establish a rigorous framework for developing a fundamental mechanistic understanding of chemical reactions catalyzed by heterogeneous catalysts. First, and through an iterative process between these three components of our research, we demonstrate unique insights derived on the nature of the active site. Then, based on that understanding, and insights derived for the importance of atomic-scale structure sensitivity, we show how we can provide guidance to inorganic synthesis for preparing alloys, which are predicted to hold promise for improved activity and selectivity for the reactions of interest.

### 5:00pm **HC+SS-TuA9 $CO_2$ Hydrogenation on Defect-Laden Hexagonal Boron Nitride**

***Tao Jiang***, *T.B. Rawal, D. Le, R. Blair, T.S. Rahman*, University of Central Florida

Defect-laden hexagonal boron nitride (*dh*-BN) has recently been shown [1] to be an excellent metal-free hydrogenation catalyst. Here, we employ density functional theory based calculations, including van der Waals interaction, to examine the reactivity of single layer *dh*-BN with N vacancy ($V_N$) or N substitution by B ($B_N$), toward the $CO_2$ hydrogenation to alcohols. To begin with, we find that $CO_2$ binds strongly at the B sites (near the vacancy) with binding energy of 1.66 eV. Next, we find that formic acid, an important reaction intermediate, chemisorbs molecularly on *dh*-BN with these defects ($V_N$ and $B_N$) with adsorption energy of -1.82 eV and -0.83 eV, respectively. Through detailed comparison of the adsorption geometries and energetics of the various reactants and intermediates, we conclude that *dh*-BN with $V_N$ defect, rather than $B_N$, is more suitable a catalyst for purposes here. The potential energy for the decomposition of formic acid ($HCOOH \rightarrow HCO + OH$) on *dh*-BN with $V_N$ is found to be -1.12 eV, indicating an exothermic reaction. The activation barrier for this reaction turns out to be 0.39 eV. We present the reaction pathways and their energetics for further hydrogenation of formic acid to form methanol or to dissociate into CO and $H_2O$. Reaction rates and turn over frequencies are next calculated using kinetic Monte Carlo simulations to obtain evaluate the propensity of *dh*-BN to serve as a catalyst for $CO_2$ hydrogenation.

[1] D. Nash et al., ACS Omega, 1, 1343 (2016).

Work supported in part by NSF grant CHE-1465105.

### 5:20pm **HC+SS-TuA10 Interaction of Atomic Oxygen with Ag(111) and Ag(110) Surfaces: Oxygen Adsorption and Kinetics at Surface versus Subsurface**

***Sara Isbill***, *S. Roy*, University of Tennessee

Transition metals are commonly used to catalyze transformations of small organic compounds, but the mechanisms of these catalytic reactions are not yet completely understood. Silver surfaces are important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards revealing the complex chemical pathways of oxidation reactions on silver surfaces, the role of subsurface oxygen (oxygen adsorbed just beneath the surface) in surface reconstruction and oxidative catalysis by silver has yet to be elucidated. Does subsurface oxygen affect catalysis by changing the electronic and geometric properties of silver, or does it emerge to the surface to directly interact with reactants? Does it initiate or promote surface reconstructions of silver? Does the participation of subsurface oxygen change with reaction conditions, such as surface structure, surface temperature, and oxygen coverage? Answers to such questions will promote a deeper mechanistic understanding of heterogeneous catalysis by silver, and help to design more effective industrial catalysts. In the present study, density functional theory (DFT) was used to probe the interactions of atomic oxygen with the surface and subsurface of Ag(111) and Ag(110) surfaces. The goal was to investigate the adsorption and kinetics of surface and subsurface oxygen at different coverages on the metal surfaces, and examine their effects on the structural and catalytic properties of silver. On the Ag(111) surface, it was found that both surface and subsurface adsorption energies decreased with oxygen coverage, but surface adsorption weakened more drastically than subsurface adsorption, resulting in oxygen binding more strongly to the subsurface than to the surface at coverages above 0.5 ML. In contrast, surface adsorption remained stronger than subsurface adsorption at higher coverages on the Ag(110) surface. Calculations also show that kinetic barriers for formation of subsurface oxygen or its emergence into the surface are strongly dependent on coverage, indicating that the direct participation of subsurface oxygen in catalysis might strongly depend on coverage. Overall, our results provide valuable insight into the competition between adsorption and kinetics of oxygen on different facets of the silver surface, the importance of charge transfer in the binding and motion of atomic oxygen on silver, and the role of subsurface oxygen in catalysis by silver.

### 5:40pm **HC+SS-TuA11 Electronic Structure and Catalytic Properties of Au/h-BN Composite System**

***Takat Rawal***, *T. Jiang, D. Le*, University of Central Florida, *P.A. Dowben*, University of Nebraska - Lincoln, *T.S. Rahman*, University of Central Florida

Rational designing of functionalized materials owning superior properties than those of their constituents is of great importance for potential applications. Herein, we study the electronic structure and catalytic properties of subnanometer sized gold nanoparticle ($Au_{13}$) supported on hexagonal boron nitride (h-BN) with single boron vacancy, employing density functional theory including van der Waals (vdW) interaction. The electronic interaction between $Au_{13}$ and h-BN is strongly facilitated by the formation of covalent bonds between an Au atom and three N atoms (the first-nearest neighbors of B vacancy), giving rise to the frontier states (near Fermi energy), which spatially distribute around the corner Au atoms as well as the Au atom that occupies the B vacancy site. We examine CO oxidation, as a prototype reaction, on $Au_{13}$/h-BN via the peroxo-type (OOCO) reaction path. Our results reveal that the highly active sites for CO activation are the corner Au atoms where the frontier states are localized. The strong affinity of CO to bind at those sites, with binding energy of 0.84 eV, can also be understood in terms of the negatively charged Au atoms. The reaction energy and the activation barriers for the reaction OOCO*’ $CO_2$(g)+O*, are found to be -2.28 eV and 0.10 eV, respectively whereas they are -1.89 eV and 0.12 eV for the reaction CO*+O*’ $CO_2$(g). These results suggest that Au/h-BN composite can catalyze the CO oxidation even at the low temperature.

Work is supported by DOE grant DE-FG02-07ER15842.

## 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

[5] Kim *et al.*, Phys. Rev. B 80 (2009) 035116

[6] Noh *et al.*, Phys. Rev. Lett. 102 (2009) 256404

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.

[1] D. Xiao *et al.*, Phys. Rev. Lett. **108**, 196802 (2012)

[2] S.D. Stolwijk *et al.*, Rev. Sci. Instrum. **85**, 013306 (2014)

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

[4] A. Bruix *et al.* Phys. Rev. B **93**, 165422 (2016)

[5] A. Grubišic Cabo *et al.*, Nano Lett. **15**, 5883 (2015)

5:40pm **MI+2D+AC+NS-TuA11 Unraveling the Spin Structure of Unoccupied States in $Bi_2Se_3$**, ***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 $Bi_2Se_3$ [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 $Bi_2Se_3$.

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

## Nanometer-scale Science and Technology Division Room: 19 - Session NS+EM+MN+PS+SS-TuA

## Nano-Photonics, Plasmonics and Mechanics

**Moderators:** Joshua Ballard, Zyvex Labs, Christian Zorman, Case Western Reserve University

2:20pm **NS+EM+MN+PS+SS-TuA1 Nonlinear Interactions of Coupled MEMS Cantilevers**, ***Christopher Wallin***, National Institute of Standards and Technology, Center for Nanoscale Science and Technology, *R. De Alba, D.A. Westly*, NIST/CNST, *S. Grutzik*, Sandia National Laboratories, *A.T. Zehnder, R.H. Rand*, Cornell University, *V.A. Aksyuk*, NIST/CNST, *S. Krylov*, Tel Aviv University, Israel, *B.R. Ilic*, NIST/CNST

Micro- and nano-electromechanical systems (M/NEMS) offer tremendous opportunities for technological advancement in mechanical resonator applications including mass, force and energy sensing, microwave amplification, optomechanics, and energy harvesting. These M/NEMS resonators have many favorable qualities including high mechanical quality factors and compatibility with integrated circuit architectures. More specifically, nonlinear, coupled M/NEMS resonating cantilever arrays have been shown to possess complex system dynamics such as intrinsically localized modes, wave propagation, and sensitivity to defects. The collective behavior of these nonlinear interacting cantilever arrays is remarkably sensitive to the slightest perturbation which makes them an excellent candidate for ultra-sensitive sensors. Moreover, custom device responses can be achieved by tuning the electrostatic fringing field coupling, altering the mechanical coupling via the device's overhang, or by introducing precisely engineered structural imperfections into the arrays. With our work, we have found that the cantilever arrays exhibit distinct propagation bands, abrupt transitions between standing wave patterns, and synchronization.

Various device geometries including interdigitated arrays, opposing element arrays, and di-element arrays were constructed using both silicon and silicon nitride as device layers. The arrays generally consisted of 100 cantilevers or more which limited boundary effects in the devices. Gold electrodes were patterned on top of the cantilevers for parametric electrical actuation and for fringing field electrostatic coupling between adjacent cantilevers. Mechanical coupling in the arrays was achieved through the large overhangs produced during the device release. The amplitude envelope of the out of plane motion of the cantilevers was captured using a CMOS camera using a frame rate of 30 $s^{-1}$. The devices were driven electrically and using a piezoelectric transducer under ambient and vacuum conditions. Large, nonlinear vibrational amplitudes were observed in the arrays along with hysteresis. The cantilever arrays exhibited unique standing wave patterns which were sensitive to defects and external loading. Since the dynamics of M/NEMS coupled cantilevers are highly sensitive to local changes in their environment, we envision the practical implementation of coupled arrays for ultra-sensitive chemical, biological, and force sensors in the future.

2:40pm **NS+EM+MN+PS+SS-TuA2 Silicon Carbonitride Nanoresonator Arrays for Proteomic Analysis**, *W. Zheng*, University of Alberta, Canada, *R. Du*, University of Alberta and The National Institute for Nanotechnology, *Y. Cao*, University of Alberta and The National Institute for Nanotechnology, Canada, *M.A. Mohammad, S.K. Dew*, University of Alberta, Canada, *M.T. McDermott*, University of Alberta and The National Institute for Nanotechnology, ***Stephane Evoy***, University of Alberta, Canada

Analysis of biological molecules is vital in many fundamental problems of molecular biology. ELISA is a widely employed array-based technique for the parallel analysis of biological analystes. This technique however requires fluorescent tagging, which may disrupt the biochemical properties being investigated. Other platforms such as quartz crystal microbalance (QCM) and surface plasmon resonance sensors (SPR) offer alternatives for the analysis of molecular mixtures. However, these platforms are not readily scalable towards large arrays. Resonant mechanical sensors operate by monitoring shifts of resonance frequencies associated to the binding. Such approach enables the frequency modulation of the output, improving the stability/noise-immunity of the reading. In addition, the adsorption sensitivity per unit area of resonators scales favourably as their dimensions are reduced, offering a compelling path for the development large arrays with exquisite mass-sensitivities.

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* **Falicov Student Award Finalist**

Suspended silicon resonators as narrow as 45 nm were initially reported by Carr, Evoy et al.[1] The brittle properties of this material however limited the yield of these structures to less than 25 %, precluding their use in large arrays. We have recently reinvented the overall approach employed in NEMS fabrication. This new approach combines surface and bulk machining techniques for the release of the device, as opposed to the widely-accepted sacrificial layer approach. We are now routinely fabricating ultra-large arrays of SiCN nanostring resonators as narrow as 8 nm and a yield approaching 100%. These are the narrowest devices produced by any machining method. Each device offers a detection threshold as small as 200 Da. These arrays have successfully been employed for the detection and analysis of protein mixtures. Diazonium modification was developed onto the SiCN surfaces and validated by X-ray photoelectron spectroscopy. Similarly modified nanostrings were then covalently functionalized with anti-rabbit IgG as molecular probe. Specific enumeration of rabbit IgG was successfully performed through observation of downshifts of resonant frequencies. The specificity of this enumeration was confirmed through proper negative control experiments. Helium ion microscopy further verified the successful functionalization of nanostrings.

[1] D. W. Carr, S. Evoy, L. Sekaric, H. G. Craighead, J. M. Parpia, App. Phys. Lett. 75, 920 (1999).

### 3:00pm **NS+EM+MN+PS+SS-TuA3 Cavity Optomechanical Coupling in Chip-Scale Plasmonic and Photonic Transducers for Nanoscale Measurements and Optical Signal Control**, ***Vladimir A. Aksyuk***, *S. An*, NIST Center for Nanoscale Science and Technology, *B. Dennis*, Rutgers University and NIST CNST, *T. Michels, B.J. Roxworthy, J. Zou*, NIST Center for Nanoscale Science and Technology **INVITED**

Devices controlling light via mechanical motion are ubiquitous, from a simple camera's zoom lens to arrays of moving mirrors correcting for atmospheric distortions in telescopes and digitally projecting movies on the cinema screens. The same optomechanical coupling provides one of the best known techniques for measuring mechanical motion, covering length scales form atomic force microscopy to kilometer scale LIGO interferometers to the red shift measurements over billions of light years. We study optomechanical coupling in micro and nanoscale systems that combine electromechanics with photonics and plasmonics, and apply such chip based optomechanical transducers to solve nanoscale measurement problems. In one example, integrated cavity-optomechanical sensing breaks the common trade-off between sensitivity and bandwidth in atomic force microscopy, allowing extremely low noise motion readout of very fast, nanoscale/picogram mechanical probes. Reducing the probe size not only increases the transduction bandwidth, but also reduces drag and therefore the fundamental thermodynamic force noise when operating in air. Even though the cantilever crossection is much smaller than the optical wavelength, the near-filed coupled high quality factor photonic cavity makes our motion readout exquisitely sensitive. As a second example, I will discuss nanomechanical plasmonic systems, where extreme confinement of the gap plasmon optical modes leads to some of the largest optomechanical coupling coefficients ever observed. I will present electro-mechanical gap plasmon phase modulators and nanomechanically tunable deep subwavelength gap plasmon resonators with potential applications for motion metrology, novel nanoscale sensing and signal transduction and arbitrary wavefront control via nanoelectromechanically tunable optical metasurfaces.

### 4:20pm **NS+EM+MN+PS+SS-TuA7 An Active Plasmomechanical System for Optical Modulation and Mechanical Lasing**, ***Brian Roxworthy***, *V.A. Aksyuk*, NIST

Plasmonic structures can couple electromagnetic radiation into volumes much smaller than the limits imposed by diffraction. This strong confinement of light transforms these static metallic nanostructures into sensitive bio-chemical sensors, near-field probes for imaging, nanoscale light sources, and effective optical tweezers [1-4]. Advancing the plasmonics paradigm to include active devices, whose resonant properties can be dynamically tuned *via* various electrical, mechanical, or thermal inputs, has great potential to advance nanoscale optical sensing and transduction and for building functional metamaterial devices [5,6].

We present a tunable plasmomechanical system that couples the localized gap plasmon (LGP) resonances of individual subwavelength structures to mechanical, electrical, and thermal modes. By engineering extremely strong optomechanical coupling of the LGPs, we achieve broad tuning of the localized resonances at megahertz frequencies using small voltages < 5 V, producing $\approx$ 40 % amplitude in the far field and $> \pi$ phase shift of the re-radiated light. We furthermore show selective, sub-diffraction optical transduction of nanomechanical motion with < 10 fm $Hz^{-1/2}$ sensitivity. Coupling of LGPs to thermal modes results in strong thermomechanical backaction capable of driving regenerative mechanical oscillations of cantilever devices – mechanical lasing – using an isolated, subwavelength plasmonic element. Our platform opens the door to smart metamaterials having programmed responses across physical domains, tunable metasurfaces and optical components, and studying optically-powered nonlinear nanomechanics.

[1] J. Anker *et al.*, Nat. Mater. 7, 442–453 (2008).

[2] D. K. Gramotnev and S. I. Bozhevolnyi, Nat. Photon., 83–91 (2010)

[3] Y-J. Lu *et al.,* Science 337, 450–453 (2012)

[4] B. J. Roxworthy *et al.,* Nano Lett. 12, 794–801 (2012)

[5] N. Zheludev and E. Plum, Nat. Nanotech. 11, 16–22 (2016).

[6] B. J. Roxworthy and V. A. Aksyuk, Nat. Commun. 7, 13746 (2016).

### 4:40pm **NS+EM+MN+PS+SS-TuA8 Plasmon-enhanced Photo-catalysis Using Collapsible Nano-fingers**, ***Yunxiang Wang***, *B. Song, W. Wu, S. Cronin*, University of Southern California

#### 1. Introduction

Photocatalytic decomposition plays an important role in the treatment of pollutants. It utilizes light radiation to decompose contaminants into non-toxic substances. While $TiO_2$ is one of the most widely used photocatalysts, visible light can hardly be used to drive $TiO_2$ due to the short wavelength cutoff of $TiO_2$. Plasmon-enhanced photo-catalysis can extend the wavelength range due to higher order effects. However, previously reported work has limited efficiency, because the hot spots were not optimized and the $TiO_2$ located outside the hottest part of the hotspots. Here, we invented a technology to fabricate collapsible nano-fingers to achieve large-area high density optimized hotspots with $TiO_2$ film located at the hottest part of the hotspots. We demonstrated highest photo-catalysis efficiency that we are aware of.

#### 2. Device fabrication

First, pillar arrays were patterned on the top two layers using UV-curable nanoimprint lithography (NIL) and reactive ion etch (RIE), as shown in Fig. 1(a) (b) (c). Au film was deposited on the sample followed by lift-off process to form gold nanoparticle arrays with diameter of 50 nm and pitch of 200 nm on the bottom layer, as shown in Fig. 1(d) (e). After nano-fingers were fabricated using RIE, 2 nm TiO2 film was deposited on the sample using atomic layer deposition (ALD), as shown in Fig. 1(f) (g). After the arrays were exposed to ethanol solutions and air-dried, the fingers closed together in groups of two or four. The scanning electron microscopic (SEM) image of the collapsed nano-fingers is shown in Fig. 2.

#### 3. Results and Discussion

The photocatalytic activities were tested using methyl orange (MO) photodegradation as the model reaction. The decay in absorbance of the solution was monitored by Varian Cary 50 UV–Vis spectrophotometer after 8 h exposure to green laser (532 nm, 3 W) irradiation. MO solution and sample were added into a standard quartz cuvette sealed with a sealing film.

The absorption spectra taken before and after irradiating are used to quantify the photocatalytic decomposition rate, as shown in Fig. 3. As a control experiment, we firstly performed experiment under same illumination condition with a silicon wafer coated with 2nm $TiO_2$ film, no MO photodecomposition was observed even after 12 h irradiation. For the monomers, the absorption of the MO solution is observed to drop by 4.9% after 8 h illumination. However, with collapsed sample, a 30% reduction in the MO absorbance is observed. This over 6-fold enhancement demonstrates a stronger plasmonic enhancement after nano-fingers being collapsed, which means this novel structure is a great platform to study plasmonic enhancement.

### 5:40pm **NS+EM+MN+PS+SS-TuA11 Ultra-High Resolution Photonics-based Thermometry**, ***Nikolai Klimov***, *T. Herman, K.O. Douglass, M.J. Chojnacky, Z. Ahmed*, National Institute of Standards and Technology

Temperature measurements play a crucial role in various aspects of modern technology ranging from medicine and manufacturing process control, to environmental and oil-and-gas industry. Among various temperature measurement solutions, resistance-based thermometry is a time-tested method of disseminating temperature standards [1]. Although industrial resistance thermometers can routinely measure temperatures with uncertainties of 10 mK, their performance is sensitive to multiple environmental variables such as mechanical shock, thermal stress and humidity. Drift of sensor resistance over time necessitates expensive, time-consuming recalibrations using ultra-sensitive reference thermometers. These fundamental limitations of resistance thermometry, as well as the desire to reduce sensor ownership cost have ignited a substantial interest in the development of alternative temperature measurement solutions such as photonics-based temperature sensors. A wide variety of innovative photonic sensors have been proposed recently including functionalized dyes [2], hydrogels [3], fiber optics-based sensors [4], and silicon micro- and nanophotonic devices [5,6]. These innovative temperature sensors have the potential to leverage advances in frequency metrology to provide cost-effective measurement solutions. Here we present the results of our efforts in developing novel on-chip integrated silicon photonic temperature sensors with nanoscale footprint and ultra-high resolution as an alternative solution to legacy-based resistance thermometers. These sensors are Fabry-Perrot cavity type silicon photonic devices that are based on photonic crystal nanobeam cavity (PhCC), whose high-Q resonant frequency mode is highly sensitive to even ultra-small temperature variations. In this talk we describe nanofabrication, fiber coupling and packaging of these thermometers, as well as their performance. We will present a direct comparison of our photonic thermometers to Standard Platinum Resistance Thermometers, the best in class resistance temperature sensors used to disseminate the International Temperature Scale of 1990. The preliminary results indicate that our PhCC nanothermometers are capable of detecting changes of temperature as small as 10 µK and can achieve measurement capabilities that are on-par or even better than the state-of-the-art resistance thermometry.

[1] Strouse, NIST Spec. Publ. 250, 81 (2008).

[2] Donner et al., Nano Lett. 12, 2107 (2012).

[3] Ahmed, J. Adv. Res. 6, 105 (2015).

[4] Kersey et al., IEEE Photonics Technol. Lett. 4, 1183 (1992).

[5] Kim et al., Opt. Express 18, 22215 (2010).

[6] Klimov et al., Proc. SPIE 9486, 948609 (2015).

6:00pm **NS+EM+MN+PS+SS-TuA12 Size-Controlled Synthesis of Gold Nanostars and their Excellent SERS and Fluorescence Quenching Properties**, ***Waqqar Ahmed***, *H.I. Khan, M.U. Khalid*, COMSATS Institute of Information Technology Islamabad, Pakistan

Noble metal nanoparticles have attracted great attention recently owing to their fascinating optical properties. They work as nanoscopic antennas by amplifying the incident and scattered electromagnetic beam. The incident electromagnetic radiation can excite the surface plasmons of nanoparticles, leading to the confinement of electromagnetic energy around the nanoparticles. This makes the metallic nanoparticles an excellent candidate for the surface enhanced Raman scattering (SERS) applications. Anisotorpic nanoparticles such as nanostars are much superior for SERS applications over their spherical counterparts owing to the special surface morphology.

We have developed a facile method for the synthesis of gold nanostars with tunable sizes ranging from 50nm to about 1µm. To the best of our knowledge, this is the widest size range reported for gold nanostars. More importantly, we have observed that these nanostars are excellent for SERS based detection owing to their large enhancement factors and efficient fluorescence quenching properties. Fluorescence is known to interfere with and overshadow the SERS signal, thus affecting the trace detection capabilities of SERS. Therefore, usually off resonance excitation lasers must be used for SERS studies of fluorophores, which limits the universal applicability of the SERS technique. We believe that non-compact surfactant coating of nanostars in our case give the target fluorophores access to nanostar's surface, thus enabling the quenching of fluorescence through Förster resonance energy transfer (FRET). The absence of fluorescence background markedly enhances the appearance of Raman peaks. We were able to achieve a limit of detection of 10pM using an excitation laser source in resonance with the electronic excitation of the target fluoropore. This makes gold nanostars universal substrates for SERS based trace detection.

## Plasma Science and Technology Division
## Room: Ballroom B - Session PS+SS-TuA

## The Science of Plasmas and Surfaces: Commemorating the Career of Harold Winters (ALL INVITED SESSION)

**Moderators:** Sumit Agarwal, Colorado School of Mines, Selma Mededovic, Clarkson University

2:20pm **PS+SS-TuA1 History and Legacy of the Coburn and Winters Paper**, ***R.Mohan Sankaran***, Case Western Reserve University, *M.C.M. van de Sanden*, FOM Institute DIFFER, Netherlands

The Coburn and Winters paper[1] is a hallmark contribution in the field of plasma processing. The study revealed very simply and cleverly the role of a plasma in reactive ion etching. When a silicon (Si) surface was exposed to an argon (Ar) ion beam alone or xenon difluoride ($XeF_2$) alone, the etch rate was found to be negligible. This showed that physical sputtering and chemical etching in the former and latter cases, respectively, could not effectively etch Si. In stark contrast, combining the Ar ion beam and $XeF_2$ resulted in a significantly higher etch rate, underscoring the synergistic mechanism of fluorine radicals reacting with the Si surface and Ar ions bombarding and kicking them off to ultimately remove Si atoms. The legacy of these experiments is not only the technological impact it has had on applications of plasma processes to semiconductor manufacturing, but, more broadly speaking, the foundation it has laid for plasma science by demonstrating how a complex system can be unraveled to yield simple correlations. This is reflected here every year at AVS where the etching sessions continue to be the largest of all the sessions in the Plasma Science and Technology Division. In this introductory talk to the session commemorating Harold Winters, a history of the Coburns and Winters experiment and its impact on plasma science and technology will be presented.

1. J. W. Coburn and H. F. Winters, *J. Appl. Phys.***50**, 3189 (1979).

2:40pm **PS+SS-TuA2 The Reaction of Fluorine Atoms with Silicon: Controversies 38 Years in the Making**, ***Vincent M. Donnelly***, University of Houston

Chemical etching of silicon by fluorine atoms in the absence of ion bombardment is reviewed. Controversies on the identity of etching products and reaction probabilities are discussed. Attempts are made to explain the apparent presence of $SiF_2$ as a primary product in many studies, dating back to 1980, but not in others, including those of Harold Winters from as early as 1979. Reported estimates of reaction probabilities (here defined as the probability of removing a Si atom from the substrate per incident F atom) vary by a factor of 2000. When these values, with some corrections and normalizations applied, are plotted as a function of F atom flux, most of them fall on a "universal curve" that reveals a large (~30-fold) decrease in the reaction probability with increasing F flux, from 0.03 at a F flux $10^{12}cm^{-2}s^{-1}$ to 0.001 at a flux of $10^{20}$ $cm^{-2}s^{-1}$. These values were extracted from beam experiments with F atoms generated from cracking of $F_2$, including those by Harold Winters, from isotropic etching in plasma experiments (both in-plasma and downstream) with $F_2$, $CF_4/10\%O_2$, and $NF_3$ feed gases, as well as from molecular dynamics simulations. Reaction coefficients derived from chemical etching rates in $SF_6$ plasmas do not follow this trend, however, suggesting a large enhancement in the F reaction probability (~20 to 100-fold at F fluxes of $10^{18}$-$10^{19}cm^{-2}s^{-1}$), due to the presence of sulfur.

3:00pm **PS+SS-TuA3 The Long Quest to Understand Etch Mechanisms and Surface Science: The Legacy of Harold Winters and its Impact on Semiconductor Industry**, ***Sebastian Engelmann***, *N.C.M. Fuller*, IBM Research Division, T.J. Watson Research Center

From the beginning of its days in semiconductor industry until now, Harold Winters work has very big impact to plasma processes and surface science. Starting with his landmark papers in the 1970's and 1980's, much scientific work was inspired by his publications. At IBM itself and industry-wide, many projects were impacted by his work. We will present our view on some of these topics as well as the lasting technological impact that Harold's work had and it inspired.

3:20pm **PS+SS-TuA4 Surface Science Aspects of (Plasma) ALD reactions**, *V. Vandalon, M.C.M. van de Sanden*, ***Erwin Kessels***, Eindhoven University of Technology, The Netherlands

The profound contributions of Harald Winters and John Coburn to the field of plasma etching have inspired us at the Eindhoven University of Technology to study the surface-science aspects of plasma deposition. The latter has been an overarching theme within our research in the last two decades. It started with investigations of the growth mechanism of amorphous carbon and silicon films prepared by plasma-enhanced chemical vapor deposition (PECVD) and it resulted even in beam-experiment-type studies using advanced real-time diagnostic probes in a dedicated high vacuum reactor [1]. The interest in understanding the surface reactions during film growth was also the motivation to step into the field of atomic layer deposition (ALD). ALD film growth is truly ruled by surface chemistry and, inspired by work of others, we recognized that the ALD field could greatly benefit from plasma-assisted processes [2]. Like in other cases of (plasma-based) film growth, a detailed understanding of the surface-science aspects is key to take advantage of all opportunities the method provides. This has been the driver for many experimental studies of the film growth by thermal and plasma ALD using a wide variety of gas phase and surface diagnostics [3]. It has also been the trigger to set up nonlinear optical studies of the surface processes during ALD, culminating in advanced broadband sum-frequency generation (SFG) studies [4]. In this contribution, the historical perspective of our research will be sketched and some recent highlights will be presented.

[1] See for example, J.J.H. Gielis *et al*., Phys. Rev. B 77, 205329 (2008).

[2] See the review paper by H.B. Profijt *et al*., J. Vac. Sci. Technol. A. 29, 050801 (2011).

[3] See for example, Heil *et al*., Appl. Phys. Lett. 89, 131505 (2006) and Langereis *et al*., Appl. Phys. Lett. 92, 231904 (2008).

[4] See for example V. Vandalon and W.M.M. Kessels, Appl. Phys. Lett. 108, 011607 (2016).

### 4:20pm **PS+SS-TuA7 Harold Winters and Plasma-Surface Interactions**, ***David Graves***, University of California at Berkeley

My trajectory in studying plasma-surface interactions was profoundly affected first by reading the papers of Harold Winters, then by talking and working with him. My co-workers and I read and re-read Harold's papers (often co-authored with John Coburn) and the insights we gained from this work had a huge impact on what we chose to investigate and how we interpreted our results. In particular, our early studies of plasma-surface interactions using molecular dynamics simulations were almost completely motivated and guided by his work. Later, I had the extraordinary good fortune to welcome Harold into my laboratory for several years as a visiting scholar. His presence (and that of John Coburn and Dave Fraser) enlightened, instructed and inspired my entire group. I will summarize the impact of Harold's scientific work, his gracious and generous personality and his innate enthusiasm for science on me and my research group.

### 4:40pm **PS+SS-TuA8 Illuminating the Black Box: Plasma-Surface Interactions at the Atomic Scale**, ***Jane Chang***, UCLA

This talk pays tributes to Harold Winters's seminal contributions in the field of plasma etching of silicon-based materials and metals. Inspired by one of the earliest papers of Harold Winters, where he presented a framework for understanding plasma etching by treating the plasma as a "pseudo-black-box" to provide a semi-quantitative understanding of plasma etching effects such as loading, this talk presents a generalized methodology, combining thermodynamic assessment and kinetic verification of surface reactions, to further illuminate the black box in an effort to tailor plasma-surface interactions for a wide range of materials. This talk does not attempt to review all of Harold Winters's work but focus on his work in metal etch and how that foundational knowledge helps guide the fundamental research in these areas to further advancements in tailoring the plasma-surface interactions to achieve desirable etch efficacy and selectivity of metals at the atomic scale.

### 5:00pm **PS+SS-TuA9 Controlling Low Temperature Plasma Surface Interactions for Atomic Layer Etching of Electronic Materials And Atmospheric Pressure Plasma-Treatments of Model Polymers and Biomolecules**, ***Gottlieb S. Oehrlein***, University of Maryland, College Park

Harold Winters's pioneering work on the scientific understanding of plasma-surface interactions, in particular as applied to low temperature plasma-based etching of materials, much of it done in collaboration with John Coburn,[1] has become textbook material. As a colleague at IBM Research I had the opportunity to learn from Harold by discussing with him ideas on rate limiting factors in etching reactions, in particular the role of surface reaction layers and the role of ion bombardment. These topics were of great interest to him as a possible explanation of ion-neutral synergy and also of the doping effect of silicon etching. In this talk I will discuss the relationship of Harold's work to topics in my own research, in particular to recent work performed by members of my group. These include atomic layer etching of $SiO_2$ and other materials[2] and interaction of the effluent of atmospheric pressure plasma sources with polymers and biomolecules.[3]

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* I gratefully acknowledge the contributions and collaboration of D. Metzler, Kang-Yi Lin, C. Li, S. Engelmann, R. Bruce, E. Joseph, E. A. J. Bartis, A. J. Knoll, P. Luan, J. Seog, V. S. S. K. Kondeti, P. J. Bruggeman and D. Graves to some of the topics in this talk. Additionally, funding from National Science Foundation (CBET-1134273, PHY-1004256, PHY-1415353), US Department of Energy (DE-SC0001939) and Semiconductor Research Corporation (No. 2017-NM-2726) is thankfully acknowledged.

### 5:20pm **PS+SS-TuA10 H-induced Defect Kinetics in a-Si:H: Obtaining Kinetic Parameters from Temperature-Dependent Data**, *F.J.J. Peeters*, DIFFER, Netherlands, *J. Zheng*, Peking University, China, *I.G.M. Aarts*, ASML, *A.C.R. Pipino*, ONR, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands, ***Richard van de Sanden***, DIFFER, Netherlands

Near-IR Evanescent-Wave Cavity Ring-Down Spectroscopy (EW-CRDS) has been applied to study the defect evolution in an a-Si:H thin film subjected to a calibrated directed beam of atomic H at different substrate temperatures (80 to 200 °C) . To this end a 42 ± 2 nm a-Si:H film was grown on the Total Internal Reflection (TIR) surface of a folded miniature optical resonator by Hot-Wire Chemical Vapor Deposition (HW-CVD). A fully reversible defect creation process is observed, with a non-linear dependence on H flux, with a time resolution of 33 ms and a relative sensitivity of $10^{-7}$. Through the use of polarizing optics the CRDS signal was split into *s*- and *p*-polarized components, which, combined with *E*-field calculations, provides depth sensitivity. Extensive kinetic modeling of the observed process is used to determine rate constants for the hydrogen-material interactions and defect formation in a-Si:H, as well as revealing a high diffusion coefficient for atomic H on the order of $10^{-11}$ $cm^2s^{-1}$. A novel reaction pathway is proposed whereby H inserted into weak Si-Si bonds recombines with mobile H, resulting in a limited penetration depth for atomic H from the gas-phase on the order of 15 nm. The defect evolution kinetics can be modeled based on a quasi-steady-state approximation of H atoms, which assumes that the H density in the film reaches a quasi-steady-state very rapidly and exhibits little change with time. This approximation significantly simplifies the kinetic model, accurately predicts the initial absorption change behavior and allows quantitative evaluation of the kinetic parameters of the microscopic processes and the corresponding activation energies.

### 5:40pm **PS+SS-TuA11 Translating Fundamental Science to Technology Development in Plasma Assisted Materials Processing: Contributions by Harold Winters and Their Impact on Modeling**, ***Mark Kushner***, *C.M. Huard, S.J. Lanham, S. Huang, P. Tian*, University of Michigan

A hallmark of the contributions of Harold Winters to the advancement of plasma materials processing is beginning with fundamental processes, and building upon this foundational knowledge towards technology development. His contributions to our understanding of ion assisted chemical sputtering, adsorption, desorption, chemisorption, conductance in features, stopping distances, mixing layers and electron impact dissociation cross sections are examples of producing foundational knowledge which enabled the work of colleagues in the field. This enabling aspect of his work is nowhere more true than for modeling and simulation, as first principles models begin with these foundational principles. In this talk, key foundational contributions by Harold Winters in plasma-surface interactions and electron impact processes will be reviewed from the perspective of enabling first principles modeling. Examples will be discussed from reactor and feature scale modeling of conductor and dielectric plasma etching, with emphasis on aspect ratio dependent etching and atomic layer etching.

Work was supported by National Science Foundation, Department of Energy Office of Fusion Energy Science, Lam Research and Samsung Electronics.

### 6:00pm **PS+SS-TuA12 Extending the Legacy of Harold Winters: Probing the Energetics and Plasma-Surface Interface of Halogenated Plasmas**, ***Ellen Fisher***, Colorado State University

In the arena of halocarbon plasma chemistry, Harold Winters and co-workers performed pioneering work by extensively exploring plasma-assisted etching of semiconductor materials using a range of halogenated systems. For example, Coburn and Winters explored the role of energetic ions in plasma-assisted etching in silicon-fluorine systems, studying the dynamic interplay between physical and chemical sputtering. This work has inspired several decades of work on halogenated plasma systems, including further elucidation of the role of ions and other energetic species within plasmas. In this work, energy partitioning for molecules formed from fluorinated plasma systems has been measured using laser-induced fluorescence, optical emission and broadband absorption spectroscopies. Focusing on two fluorinated species, SiF in $SiF_4$ plasmas and $CF_x$ in $C_xF_y$ fluorocarbon plasmas, we find that small molecules in these systems exhibit extremely high electronic excited state vibrational temperatures, $T_V$, relative to rotational temperatures, $T_R$. This suggests that vibrational modes are preferentially excited over other degrees of freedom. Using the imaging of radicals interacting with surfaces (IRIS) technique, surface scattering coefficients measured for each radical show a strong correlation with the associated $T_V$, with little dependence upon $T_R$or translational temperatures. This presentation will focus on plasma deposition and etching systems where understanding the relationship between the gas-phase and the resulting surface properties allows for deeper insight into creating advanced functional materials for a range of applications. Specific examples will include fluorocarbon film formation as well as production and modification of multidimensional materials.

## Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
## Room: 9 - Session SA+AS+HC+SS-TuA

### Frontiers of Photoelectron Spectroscopy: Surface & Interface Processes with Variable Depth Probe, High Spatial or Temporal Resolution
**Moderators:** Geoff Thornton, University College London, Carla Bittencourt, University of Mons, Belgium

2:20pm **SA+AS+HC+SS-TuA1 AVS 2017 Medard W. Welch Award Lecture: Ionic Liquid Surface Science**, ***Hans-Peter Steinrück****, University Erlangen-Nuernberg, Germany **INVITED**

Ionic liquids (ILs) are molten salts with a melting point below 100◦C. They represent a new class of liquid materials with unique property profiles originating from a complex interplay of Coulombic, hydrogen bonding, and van der Waals interactions of their ions. The enormous variety of cation-anion combinations enables tuning of the physico-chemical properties over a wide range. Functional groups can be implemented in their chemical structure to adapt them for specific tasks - such functionalized ILs are known as 'task-specific ionic liquids'. Applications range from catalysis and organic synthesis to tribology, protective coatings and gate dielectrics. In catalysis, two important concepts are Supported Ionic Liquid Phase (SILP) and Solid Catalyst with Ionic Liquid Layer (SCILL). In both, a high surface area solid substrate is covered with a thin IL film, which contains either a homogeneously dissolved transition metal complex for SILP, or which modifies catalytically active surface sites at the support for SCILL. The interface of the IL with the gas phase/vacuum or with the solid support plays an important role. Therefore, knowledge about surface and interface properties and their relation to the chemical structure is of pivotal importance for choosing the right IL for a specific application. In contrast to most other liquids, ionic liquids have a very low vapor pressure, and thus can be studied with the methods of ultrahigh vacuum-based surface science. One particularly powerful method is angle-resolved X-ray photoelectron spectroscopy. Thereby, detailed information on their surface composition, on segregation and enrichment effects, on the dissolution and reactivity of catalytically active metal complexes, on the growth of ultrathin IL-layers, and even on reactions in the liquid phase, can be obtained. Several examples will be discussed illustrating the power of surface science to study this new materials class. Many of the derived conclusions are considered representative for liquid surfaces in general.

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3:00pm **SA+AS+HC+SS-TuA3 *In Situ* Characterization of Semiconductor Nanowire Devices by Nano-Focus X-ray Photoemission Microscopy and Spectroscopy**, *S. McKibbin, **Andrea Troian**, S. Yngman,* Lund University, Sweden, *H. Sezen, M. Amati, L. Gregoratti,* Elettra-Sincrotrone Trieste, Italy, *A. Mikkelsen, R. Timm,* Lund University, Sweden

III-V semiconductor nanowires (NWs) have a large technological potential within electronics, optoelectronics, and energy harvesting [1,2], mainly due to their flexibility in creating heterostructures by axial stacking during epitaxial growth. Because of their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly determined by surface properties. X-ray photoemission spectroscopy (XPS) has been proven highly suitable for studying surface composition and electronic properties of homogeneous NWs [3]. However, in order to better understand NW device performance, it is essential to also investigate NW heterostructures, with nm-scale lateral resolution and during device operation.

Here, we will present nano-focus XPS results from material and doping heterostructures in InP and GaInP NWs intended for photovoltaic application [2]. We used scanning photoemission microscopy (SPEM) at the ESCAMicroscopy beamline of the ELETTRA synchrotron, providing a lateral resolution of about 120 nm, for imaging individual NWs. In addition, we revealed the change in local surface potential across (Ga)InP *pn*-junctions and InP/GaP tunnel junctions, obtained from In 3d, In 4d, and P 2p XP spectra acquired along the heterostructure NW. Electrical contacts were provided to both ends of the investigated NW, allowing to vary the source-drain bias along the NW during SPEM characterization. We will present detailed results on the influence of built-in potential and external forward and backward bias on the surface potential distribution across NW interfaces.

In another approach, we aim at revealing *in-situ* the interplay of surface chemical composition and local electronic properties. As a model system, we chose InAs NWs consisting of several segments of wurtzite and zincblende crystal structure [4]. At the interface between such segments, we confirmed a staggered type-II electronic band alignment, obtained from nano-focus XP spectra along externally biased NWs. After removing the native oxide from the NW surface by atomic hydrogen annealing [4] in the XPS UHV chamber, the same NW instead showed flat-band conditions, which is preferential for electronic application [1]. We will discuss future plans of using the dynamic high pressure option of the ESCAMicroscopy beamline for changing the surface chemistry of NWs while simultaneously investigating them with SPEM and nm-scale spectroscopy.

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[2] J. Wallentin *et al*., Science **339**, 1057 (2013).

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3:20pm **SA+AS+HC+SS-TuA4 Introducing Ionic-Current Detection for X-ray Absorption Spectroscopy in Liquid Cells**, ***Daniela Schoen***, Helmholtz-Zentrum Berlin, Germany

Photons and electrons are two common relaxation products upon X-ray absorption, enabling fluorescence yield and electron yield detections for X-ray absorption spectroscopy (XAS). The ions that are created during the electron yield process are relaxation products too, which are exploited in this study to produce ion yield for XA detection. The ionic currents measured in a liquid cell filled with water or iron(III) nitrate aqueous solutions exhibit characteristic O K-edge and Fe L-edge absorption profiles as a function of excitation energy. Application of two electrodes installed in the cell is crucial for obtaining the XA spectra of the liquids behind the membrane. Using a single electrode can only probe the species adsorbed on the membrane surface. The ionic-current detection, termed as total ion yield (TIY) in this study, also produces an undistorted Fe L-edge XA spectrum, indicating its promising role as a novel detection method for XAS in liquid cell.

5:00pm **SA+AS+HC+SS-TuA9 Non-destructive Depth Profiling of $LaAlO_3/SrTiO_3$ Interfaces**, ***Conan Weiland***, NIST, *A.K. Rumaiz,* National Synchrotron Light Source II, Brookhaven National Laboratory, *G.E. Sterbinsky,* Advanced Photon Source, Argonne National Laboratory, *J.C. Woicik,* NIST

The interface between $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) is known to be conductive, even though both LAO and STO are insulators. The interface may also host a variety of interesting phenomena such as a two-dimensional electron gas, ferromagnetism, and superconductivity. Various mechanisms have been proposed to explain the formation of the conductive interface, including the 'polar catastrophe', wherein the polar discontinuity at the interface leads to a diverging potential allowing electronic reconstruction, oxygen vacancies at the interface or at the LAO surface, and chemical intermixing, amongst others.

Synchrotron-based variable kinetic energy x-ray photoelectron spectroscopy (VKE-XPS) is a unique and powerful tool to non-destructively probe the chemical and electronic structure of buried interfaces such as that between LAO and STO. Using VKE-XPS, we have analyzed a series of LAO films on STO and have observed compositional variations in the LAO films as a function of depth: Al-enrichment occurs at the LAO surface. Additionally, an electric field was observed in some samples. In this presentation we will discuss the relevance of these results on the formation of conductive LAO/STO interfaces.

5:20pm **SA+AS+HC+SS-TuA10 Hard X-ray Photoelectron Spectroscopy Study of the Resistive Switching in Te-based Conductive Bridging Random Access Memories**, ***Munique Kazar Mendes***, *E. Martinez, O.J. Renault, R. Gassilloud, M. Bernard, M. Veillerot,* CEA/LETI-University Grenoble Alpes, France, *J.M. Ablett,* Synchrotron SOLEIL, France, *N. Barrett,* SPEC, CEA Saclay - University Paris-Saclay, France

Conductive bridging random access memories (CBRAM) are emerging devices for the next generation of non-volatile memories (NVM) (1). The CBRAM mechanism is related to ionic transport and electrochemical reactions, which give rise to the formation and dissolution of a conductive filament through the insulating dielectric layer (2). Data storage relies on

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* **Medard W. Welch Award Winner**

switching the resistivity between two high (HRS) and low (LRS) resistance states by applying voltage or current pulses. We investigate the electrochemical reactions involved in the switching mechanism of $Al_2O_3$-based CBRAMs with different active electrodes (TiTe and ZrTe) (3). We have used hard X-ray photoelectron spectroscopy to learn about electrochemical reactions involved in the switching mechanism with sufficient depth sensitivity. Photon energies of 6.9, 8.0 and 10.0 keV were chosen to obtain a non-destructive in-depth chemical characterization with varying sampling depths. The HAXPES experiments were performed at the Galaxies beamline (Soleil) on As-grown samples, after ex-situ forming (Formed) and after Reset operations. The comparison between these different resistance states shows the role and evolution of the electrode/electrolyte interfaces during electrical biasing. For the TaN/TiTe/$Al_2O_3$/Ta stack, results highlight, the reduction of Ti together with alumina oxidation after forming. The sample polarization causes oxygen migration, probably in the $O^{2-}$ form, pushed by the upper negative bias towards the interface between the active electrode and the solid electrolyte ($Al_2O_3$). When reversing the polarity of the applied voltage (Reset operation), we observe Ti reoxidation and alumina reduction, characterizing oxygen migration towards the active TiTe electrode. These results reveal the important role of oxygen migration in the filament formation/dissolution. ToF-SIMS measurements are also performed to get complementary in-depth chemical information. We will finally compare the two active electrodes to investigate the influence of the composition on the switching mechanism.

References

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3. Jameson JR, Kamalanathan D. Subquantum conductive-bridge memory. Appl Phys Lett. 2016 Feb 1;108(5):053505.

5:40pm **SA+AS+HC+SS-TuA11 Correlation of the Magnetic and Magnetotransport Properties, Electronic and Atomic Structure of Strongly Correlated Complex-oxide Thin Films with the Oxygen Vacancies and Films Thickness**, ***German Rafael Castro***, Spanish CRG BM25 Beamline at the ESRF, France, *J. Rubio Zuazo*, SpLine Spanish CRG BM25 Beamline at the ESRF, France

Herewith, we present structural, electronic, morphological and magnetotransport properties of thin films of perovskite-manganese oxides (maganites) grown on SrTiO3(001) by oxygen assisted pulsed laser deposition (PLD) methods, using Hard X-ray Photoelectron Spectroscopy (HAXPES), and Grazing Incidence X-ray diffraction (GIXRD).

Perovskite-manganese oxides exhibit a wide variety of interesting physical properties which originate from mutual coupling among spin, charge and lattice degrees of freedom. $La_{1-X}CaxMnO_3$–type perovskite-manganese oxides are strongly correlated electron systems and exhibit, in the Ca doping range between 0.15 and 0.5, a ferromagnetic–paramagnetic (FM) phase transition accompanied by a metal–insulator (MI) transition that results in a colossal magneto-resistance behaviour. In bulk $La_{0.7}Ca_{0.3}MnO_3$ (LCMO), the transition temperature TFM, TMI rises for 33% Ca doping level reaching values close to room temperature. The results shown here are focused on the study of the influence of buried interfaces and the oxygen vacancies on the electric and magnetotransport properties of $La_{0.7}Ca_{0.3}MnO_3$ thin films grown on $SrTiO_3$(001)

The growth of these materials in thin film form opens possibilities for magneto-electronic devices applications. The atomic and electronic structures, as well as the oxygen content, are followed simultaneously by GIXRD and HAXPES. Combining GIXRD, HAXPES and transport techniques, we have established a correlation between the electronic, atomic structure and magnetic and magnetotransport properties of $La_{0.7}Ca_{0.3}MnO_3$ thin films as a function of the oxygen vacancies and films thickness.

6:00pm **SA+AS+HC+SS-TuA12 Synchrotron–Based X-ray Spectroscopy Studies of Inorganic-Organic Hybrid Halide Perovskite Materials Surfaces and Properties**, ***Deidra Hodges***, *S. Shahriar, A.K. Mishra, V. Castaneda, V. Vidal, M. Martinez, N. Garcia, J. Munoz, J. Lopez*, University of Texas at El Paso

Recently, the methylammonium lead iodide $CH_3NH_3PbI_3$ perovskites have attracted a lot of attention as a possible absorber material for thin film solar cells due to their bandgap energy, high optical absorption coefficients and low-cost solution-processing deposition approaches. Methylammonium lead iodide $CH_3NH_3PbI_3$ perovskite solar cells have evolved with transformative potential with laboratory efficiencies greater than 20%. Perovskite absorber materials are very inexpensive to synthesize and simple to manufacture, making them an extremely commercially viable option. Solar cell efficiencies of devices using these materials have increased from 3.8% in 2009 to a Newport certified 20.1% in 2015, making this the fastest-advancing solar cell technology to date. These devices are known for their high photon absorptivity, tunable large direct band gaps with superior carrier charge transports, and low-cost methods of fabrication. Methylammonium lead tri-iodide $CH_3NH_3PbI_3$ perovskites thin films and single crystals were prepared for synchrotron-based X-ray spectroscopy studies of the perovskite materials surfaces and properties. The perovskite thin films and single crystals were characterized at the National Synchrotron Light Source (II) (NSLS-II) at Brookhaven National Laboratory (BNL). Synchrotron-radiation-based chemical analysis using X-ray fluorescence (XRF), and X-ray absorption near edge structure (XANES) spectroscopy were performed on samples for detailed analysis into chemical composition, stoichiometry, and material surface properties.

## 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 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

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* **NSTD Student Award Finalist**

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.

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### 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.

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 $GaCl_4$ (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.

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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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[2] Collins, Liam, et al. "Full data acquisition in Kelvin Probe Force Microscopy: Mapping dynamic electric phenomena in real space." *Scientific reports* 6 (2016): 30557.

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## Sustainability Focus Topic
## Room: 5 & 6 - Session SU+2D+MS+NS-TuA

## Membranes, Thin Films, and Sensors

**Moderators:** Keith Brown, Boston University, Roya Maboudian, University of California at Berkeley

2:20pm **SU+2D+MS+NS-TuA1 Protecting Food and Water Quality: Considerations for Materials Innovation**, ***Susan Duncan***, Virginia Polytechnic Institute and State University **INVITED**

Innovation in materials and membranes provides opportunity for enhancing water and food safety, diversifying and expanding water and food sources, protecting nutrient quality and bio-availability, and improving human health and well-being. Food and water are transitioned from their original sources into resources for animal feed and human food through production, processing, packaging, and distribution/retail stages. Throughout these stages, membranes and materials for physical and chemical separations, microbiological control, analysis and measurement, capture and containment are required.

Synergistic partnerships, among scientific disciplines and between private-public entities, encourage innovation in the design and applications of materials and membranes for discoveries and advancements in water and food processing and packaging. The objective of this discussion is to showcase the engagement of chemists, engineers, and food scientists in approaching and resolving challenges relating to water and food processing, safety, and quality and the relationship to the consumer. Three featured examples, relating to membranes and materials, include:

Aquaculture: Recirculating water for the purpose of raising fish has high economic and global impact by increasing sustainable supply of high quality food proteins for feeding the growing global population. Challenges include the need for removing biosolids, small molecular weight molecules, and bacteria that influence fish health and quality of the fish as a food source.

Water Safety from Source and Supplier to the Consumer: Protecting public health is the primary role of water treatment. Changes in water disinfectant treatment, e.g. chlorine to chloramine, affect material stability, safety and performance and can lead to significant economic impacts and consumer concerns.

Food Packaging Functionality: Protecting food and beverage freshness from processing to purchase requires understanding of the food system, the process, and storage conditions. Innovative materials that interfere with light energy can protect beverage and food quality for retaining freshness and nutrient retention for enhancing human health.

Expanding our scientific continuum from molecule to materials through process, package and consumer perspective enriches and guides scientific discovery.

3:00pm **SU+2D+MS+NS-TuA3 Real-time Detection of Water Contaminants Using a Graphene-based Field-Effect Transistor Sensing Platform**, ***Junhong Chen***, University of Wisconsin - Milwaukee **INVITED**

The National Academy of Engineering identified “providing access to clean water” as one of the top 10 grand challenges for engineering in the 21st century. A central requirement for safe drinking water is the availability of low-cost and real-time water quality monitoring. Current detection methods for critical analytes in water are often too expensive or unsuitable for in-situ and real-time detection (*an unmet need*). As a result, there is a lack of water quality monitoring along the water distribution line and at the point of use, which is inadequate because of potential deterioration in water quality within water distribution systems (e.g., Flint Water Crisis). This talk will unveil a powerful approach to real-time water sensors through a graphene-based field-effect transistor platform. The working principle of the sensor is that the conductivity of 2D nanomaterial channel (usually measured in resistance) changes upon binding of chemical or biological species to molecular probes anchored on the graphene surface. As such, the presence and the concentration of analytes, such as heavy metals, bacteria, and nutrients, can be rapidly determined by measuring the sensor resistance change. The talk will introduce the performance of the sensor for detection of various water contaminants and focus on the molecular engineering aspects of the sensor device through both theoretical and experimental approaches. The talk will end with a brief introduction on the translation of the platform technology from concept to prototype product through partnership with industries.

5:00pm **SU+2D+MS+NS-TuA9 Nanocellulose Thin Films and Nanocellulose Aerogels**, ***Kenneth Carter***, University of Massachusetts - Amherst, *A. Chang*, *K.L. Martin*, *Y. Li*, University of Massachusetts – Amherst **INVITED**

Nanocellulose is an interesting material with unique properties and chemistry. We have worked to exploit these characteristics to develop new functional thin films and aerogels. We have developed a new method for the preparation of well-dispersed cellulose nanofibrils and nanocrystals. Advantageously, the method does not require the use of harsh acids and excludes the use of catalytic oxidants such as 2,2,6,6-tetramethyl-1-piperidine-N-oxy (TEMPO) . Furthermore, the nanofibrils and nanocrystals produced by the method are easily re-dispersible and give stable aqueous dispersions. Transparent, robust nanocellulose thin films were prepared with outstanding anti-fogging properties. Most recently, nanocellulose was used to prepare aerogel/foam materials using a new fabrication method. The aerogels are mechanically stable and robust. Our new aerogel fabrication process obviates the need to use freeze-drying or low pressure solvent removal. We will present data on new nanocellulose aerogels with densities ranging from 5-100 $mg/cm^3$.

5:40pm **SU+2D+MS+NS-TuA11 Fabrication and Characterization of Thermal Treated Si/Si+Ge Thin Films For Energy Harvesting**, *S. Budak*, *Z. Xiao*, ***Michael Howard***, *B. Rodgers*, *M. Alim*, Alabama A&M University

Thermoelectric thin film devices were prepared from the alternating nanolayers of Si and Si+Ge to form the Si/Si+Ge thin films structures using DC/RF magnetron sputtering system. Fabricated thermoelectric devices were treated at different temperatures for an hour for each case to form quantum (nano) structures in the alternating nanolayers of Si and Si+Ge to increase both the Seebeck coefficients and the electrical conductivity and decrease the thermal conductivity. The prepared Si/Si+Ge thin film thermoelectric devices were characterized using the Seebeck coefficient measurement; the four probe van der Pauw resistivity measurement and the laser thermal conductivity systems for in-plane geometries. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM+EDS). Thermal treatment showed positive effects on the thermoelectric properties of Si/Si+Gethin films on the selected temperatures. The findings will be presented during the meeting.

**Acknowledgement**

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

6:00pm **SU+2D+MS+NS-TuA12 Thermoelectric Properties of $Bi_2Te_3$/$Sb_2Te_3$ Thin Films Annealed at Different Temperatures**, *S. Budak*, *Z. Xiao*, *M. Howard*, ***Breonna Rodgers***, *M. Alim*, Alabama A&M University

Thermoelectric devices were prepared from $Bi_2Te_3$/$Sb_2Te_3$ thin films using DC/RF magnetron sputtering system. Fabricated devices were annealed at different temperatures to form nanostructures in the multilayer thin films to increase both the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The thermoelectric devices were characterized using Seebeck coefficient measurement system; four probe van der Pauw measurement resistivity system and the laser thermal conductivity system. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM/EDS).

**Acknowledgement**

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

## Thin Films Division
## Room: 20 - Session TF-TuA

## ALD Precursors and Surface Reactions

**Moderators:** Qing Peng, University of Alabama, Riikka Puurunen, Aalto University, Finland

2:20pm **TF-TuA1 Accelerated Searching of Potential Precursors for Silicon Carbide-atomic Layer Deposition from Ab-initio Machine Learning Methods**, ***Zhigang Mei***, *S. Bhattacharya*, *A. Yacout*, Argonne National Laboratory

Due to the superior thermophysical properties of silicon carbide at high temperature, silicon carbide (SiC) coatings have the potential to offer excellent resistance to both oxidation and hydriding of zircaloy-based nuclear fuel cladding used in light water reactors. Unfortunately, the current deposition technique for SiC using chemical vapor deposition (CVD) can be only achieved at relatively high substrate temperatures, which can severely degrade the performance of zircaloy cladding. As a comparison, atomic layer deposition (ALD) enables the growth of pinhole free films on large and convoluted substrates with nanometer precision that operates at low temperatures. Developing a new ALD process requires better understanding of how the film growth process takes place, which depends on the chemicals being used. The major obstacle to low-temperature ALD of SiC is to determine the right precursors. To this end, we use high-throughput *ab initio* calculations and state-of-the-art machine learning (ML) techniques to accelerate the precursor screening. The method involves two different types of prediction: the forward and backward predictions. The objective of the forward prediction is to train a set of machine learning models for the free energies of silicon and carbon-containing molecules from the high-throughput *ab initio* database. Inverting the trained forward models through Bayes' law, we quantitatively predict the free energies of all the possible silicon and carbon-containing molecules from the PubChem compound database. By calculating the Gibbs energy of reaction using the ML predicted energy, several potential silicon and carbon precursors are predicted to be promising for ALD of SiC at low temperature. We believe the present method will be helpful to develop novel ALD precursors for other applications.

2:40pm **TF-TuA2 Surface Chemistry of Ru Atomic Layer Deposition Precursors**, *X. Qin*, ***Francisco Zaera***, University of California

The thermal chemistry on nickel, silicon oxide, and aluminum oxide surfaces of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium(III), a precursor used for the growth of metallic ruthenium thin films via atomic layer deposition (ALD), was characterized by using a combination of X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and reflection-absorption infrared absorption spectroscopy (RAIRS). Several intermediate steps were identified during the surface decomposition of this precursor on nickel, with the release of carbon monoxide into the gas phase, the formation of tert-butyl species on the nickel substrate, and the reduction of the metal center in stepwise fashion between approximately 300 and 500 K. ALD cycles with oxygen as the second reagent accomplish the efficient removal of all carbon contaminants from the surface and the reversible oxidation-reduction of the metal, indicating the feasibility of growing metallic films with such oxidizing reactant. However, the formation of volatile Ru oxides prevents the buildup of multilayers of the metal. Experiments with other oxidants (nitrous oxide) and other substrates show promise for finding a solution to this problem.

3:00pm **TF-TuA3 Mechanistic Aspects of ALD Ru Thin Film Growth based on $Ru(DMBD)(CO)_3$ and $H_2O$ using Downstream Quadrupole Mass Spectrometry**, ***Zhengning Gao***, Washington University in St. Louis, *R. Kanjolia*, EMD Performance Materials, *P. Banerjee*, Washington University in St. Louis

The precursor 2, 3 - dimethyl butadiene Ruthenium tri-carbonyl ($Ru(DMBD)(CO)_3$), is a volatile molecule with favorable properties for the deposition of both Ru and $RuO_2$ films via ALD.[1] An intriguing aspect of this precursor is its asymmetric molecular structure with the DMBD ligand coordinated to one side of the $Ru^{4+}$ center, while the 3 carbonyl groups are bonded to the opposite side. This makes the molecule an attractive candidate to study using *in situ* downstream quadrupole mass spectrometry (QMS) since, the release of DMBD vs. carbonyl groups during ALD half-reactions can provide a particularly descriptive view at the atomic level of how $Ru(DMBD)(CO)_3$ interacts with the substrate.

In this talk, we will discuss the mechanism of ALD of Ru thin films using $Ru(DMBD)(CO)_3$ and $H_2O$. The QMS signal of the $Ru(DMBD)(CO)_3$ consists of three distinct species. First, the mass-to-charge ratio (m/e) of 67 corresponds to the DMBD ligand dissociating from the molecule[2]. Second, a strong m/e = 16 is also observed as the DMBD further cracks into smaller fragments. Finally, m/e = 44 is observed and is related to $CO_2$ and HCOOH formation from the reaction of the tri-carbonyl groups with $H_2O$.[3] The QMS signal of these three species will be discussed in the context of varying process parameters such as Ru(DMBD)$(CO)_3$ and $H_2O$ pulse times and the temperature of the ALD process. Additionally, *ex situ* film characterization including atomic force microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectrum and resistivity measurements will be presented to correlate the process signatures obtained via QMS to the film type, morphology and electrical properties.

**References:**

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2. Chiang, C.-M.; Rowe, J.; Malic, R.; Sen, A.; Steigerwald, M.; Mills, A., A new CVD reaction for atomic layer deposition of silicon. *Applied surface science* **1996,***107*, 189-196.

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### 3:20pm **TF-TuA4 Nucleation of $Al_2O_3$ Atomic Layer Deposition with Water or $H_2O_2$**, ***Adam Hinckley***, *A.J. Muscat*, University of Arizona

Aluminum oxide ($Al_2O_3$) is a suitable replacement for $SiO_2$ in electronic devices such as flash memory due to its wide band gap and higher dielectric constant. Atomic layer deposition (ALD) using sequential pulses of trimethylaluminum (TMA) and an oxidant is a leading method for the formation of nano-scale $Al_2O_3$ layers. $Al_2O_3$ layers grown by ALD have been demonstrated with leakage currents of less than 1 nA/cm$^3$. The quality of the layers depends on both the deposition temperature and choice of oxidant, which is commonly water or oxygen atoms generated using a plasma.

An oxidant more reactive than water, such as $H_2O_2$, could produce a denser $Al_2O_3$ film. The growth of $Al_2O_3$ on hydrogen-terminated silicon using TMA and $H_2O_2$ was compared to that using TMA and water as a reference. Spectroscopic ellipsometry was used to determine the growth per cycle (GPC), and *in situ* x-ray photoelectron spectroscopy (XPS) was recorded before and after each precursor dose. The O 1s XPS peak at 531.8 eV and the Al 2p peak at 75.5 eV were used to monitor the formation of the Al-O bond and the C 1s peak at 284.5 eV was used to monitor the persistence of the Al-C bond after each half cycle. A second state in O 1s XPS at 533.3 eV assigned to the O-H bond was used to estimate the number of reactive sites present after each oxidant pulse.

The growth-per-cycle (GPC) was equal to 1.2 Å at $H_2O_2$ pulse times above 0.3 s, which is similar to reported ALD growth rates using water. The Al 2p XPS peak appeared after 4 ALD cycles using anhydrous $H_2O_2$ and after 7 cycles using water. The aluminum coverage after 10 ALD cycles was 40 % greater for anhydrous $H_2O_2$ compared to water, although the GPC was similar for each co-reactant. The O-H coverage doubled with each pulse of $H_2O_2$. The O 1s peak assigned to O-H also broadened with subsequent ALD cycles due to the presence of additional surface states. Each pulse of water increased the O-H coverage by about 1.5 times compared to the subsequent pulse. The ratio between C 1s and Si 2p peak areas showed twice as much carbon present on the surface during $H_2O_2$ ALD. The C 1s/Si 2p ratio increased during pulses of TMA and decreased during pulses of $H_2O_2$ due to surface reactions that desorb $CH_4$. Greater OH densities and C coverages indicate that $H_2O_2$ activates more surface sites for the metal precursor than water, improving $Al_2O_3$ film density.

### 4:20pm **TF-TuA7 Direct Measurements of Half-Cycle Reaction Heats during Atomic Layer Deposition Provide Mechanistic Insights**, ***Charles T. Campbell***, *J. Lownsbury*, University of Washington, *K.S. Kim, A.B.F. Martinson*, Argonne National Laboratory

We introduce here a new high-temperature adsorption calorimeter that approaches the ideal limit of a heat detector whereby the signal at any time is proportional to the heat power being delivered to the sample, and prove its sensitivity for measuring pulse-to-pulse heats of half-reactions during atomic layer deposition (ALD) at 400 K. The heat dynamics of amorphous $Al_2O_3$ growth via sequential self-limiting surface reaction of trimethylaluminum (TMA) and $H_2O$ is clearly resolved. Calibration enables quantitation of the exothermic TMA and $H_2O$ half-reactions with high precision, -343 kJ/mol TMA and -251 kJ/mol $H_2O$, respectively. A time resolution better than 1 millisecond is demonstrated, allowing for the deconvolution of at least two distinct surface reactions during TMA micro-dosing. It is further demonstrated that this method can provide the heat of reaction versus extent of reaction during each precursor's half-reaction, thus providing even richer mechanistic information on the surface processes involved. The broad applicability of this novel calorimeter is demonstrated through excellent signal-to-noise ratios of less exothermic ALD half-reactions to produce $TiO_2$ and MnO.

### 4:40pm **TF-TuA8 Cyclic Silane Precursors in Atomic and Molecular Layer Deposition**, ***Nicholas Strandwitz***, *L. Ju*, Lehigh University

Cyclic azasilanes are a promising class of reactants for atomic and molecular layer deposition due to their volatility, reactivity, and diverse set of peripheral chemical functionalities. The reactivity of this class of molecules stems from ring strain and unstable Si-N bonding. Reaction with water or OH groups results in ring opening and Si-O bond formation and is a useful chemical step for controlled film growth. This work focuses on using and understanding this class of molecules for use in atomic and molecular layer deposition ( ALD, MLD). The efficacy of the ring opening reaction and the diversity of functional groups on the cyclic azasilanes deem this precursor group highly promising for MLD. We report the growth of various MLD films based on reaction with anhydrides, metal-organics, and water. The film growth was found to be optimal near 100 °C. The two chemistries reported here are the sequential reaction of (1) a cyclic azasilane, maleic anhydride, and water and (2) a cyclic azasilane, maleic anhydride, trimethylaluminum (TMA), and water. Reaction 1 showed clear evidence of diffusion and reaction within the film as evidenced by large growth rates (~10 nm per cycle) after ~15 growth cycles, regardless of purge time. However, use of TMA in reaction 2 arrested this diffusion, presumably due to consumption of reactive groups or through densification of the film. Film properties were measured as a function of annealing temperature using ellipsometry, x-ray reflectivity, and infrared absorption measurements. These measurements indicate a densification of the films while maintaining low surface roughness. Porosity is evident after removal of organic components by a low dielectric constant for the films derived from reaction 1.These MLD chemistries offer a route to tunable hybrid thin films on high aspect ratio substrates and have potential applications in diffusion barriers, low dielectric constant layers, and passivation layers.

### 5:00pm **TF-TuA9 Area Selective Atomic Layer Deposition Via Precursor Selective Adsorption: Theory, Strategy, and Applications in Catalysis**, ***Rong Chen***, Huazhong University of Science and Technology, PR China **INVITED**

Atomic layer deposition (ALD) is a powerful thin film deposition method with precise thickness control, good uniformity, and high conformality on entire surface. While in catalysis applications, there are increasing interests for synthesis of catalysts with well-defined nanostructures, thus ALD has become a desired method for catalyst synthesis with precise control of size, composition, nanostructure, etc. Herein we report the area selective growth strategies via ALD precursor selective adsorption to obtain desired metal-oxide composite catalysts. Combining *in-situ* QCM, FTIR and DFT calculations, a series of oxide ALD precursors with $-(CH_3)_n$ $-(N(CH_3)_2)_n$, $-(Cp)_n$, and $–(thd)_n$ ligands are studied on their chemisorption and binding energies to metal surfaces. The selective growth behavior shows a strong correlation with different precursor ligands as well as the counter reactants. Thus with optimal precursor choice and reaction condition, desired nanocomposite structures could be achieved via area selective ALD.

### 5:40pm **TF-TuA11 AVS 2017 John A Thornton Memorial Award and Lecture: Atomic Layer Deposition: Highlights from the Last 25 Years**, ***Steven George****, University of Colorado at Boulder **INVITED**

The Thornton Memorial Lecture will discuss atomic layer deposition (ALD) highlights from the last 25 years. The lecture will trace the history of ALD starting with the earlier developments in atomic layer epitaxy (ALE). The presentation will recount the importance of semiconductor processing needs to the growth of ALD and the situation that led to the name change from ALE to ALD. The talk will also describe personal highlights in the development of ALD and acknowledge some of the people and circumstances behind those developments. In addition, the lecture will include commentary on the evolution of ALD. The presentation will conclude by looking ahead to the future of ALD.

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* **John A. Thornton Memorial Award Winner**

## Vacuum Technology Division
## Room: 7 & 8 - Session VT+MN-TuA

## Pumping
**Moderators:** Tamirisa Apparao, SHI Cryogenics Group, Julia Scherschligt, NIST

2:20pm **VT+MN-TuA1 Silicon-micromachined Turbomolecular Pump**, ***Wei Yang***, PD Sciences LLC **INVITED**

Deep miniaturization of sensing and analytical instruments, such as mass spectrometers, vacuum electron devices, atomic clocks, and cold atom devices, are pushing the limit of conventional vacuum packaging technologies in micro scales. Ultra-high vacuum (UHV) of $10^{-6}$ to $10^{-10}$ torr which are beyond the capability of current passive packaging technologies, have become increasingly necessary for stable operation and high performance. Although $10^{-6}$ torr and higher vacuum levels are routinely achieved in macro scale systems by passive sealing and getters, maintaining such vacuum at chip-scale has unique challenges arising from scaling laws and practical limitations. Therefore, a micro scale UHV pump is highly desirable as an enabling component for a wide range of mobile or miniature instruments.

Integration of silicon MEMS and precision metal machining offers a viable path to new capabilities unattainable in their own native environments. We will present such an accomplishment in the development of a micro turbomolecular pump that takes advantage of the high-density microstructures from silicon microfabrication, and the range of motion from a precision spindle. Major achievements include compression ratio over $10^6$ and maximum stall pressure of 100 Torr at relatively low tip speed of 120 m/s. This is a major milestone in the pursuit of moving UHV systems from laboratories to mobile platforms. Of particular significance, the successful demonstration of the molecular pumping against such a high exhaust pressure, a direct consequence of dimensional downscaling, points to the feasibility of a single-stage system from UHV to atmospheric pressure in miniature scales. We will discuss key technical challenges such as silicon fabrication, high-tolerance bonding, scaling analysis and simulation methodology, and touch on potential applications in small-scale thermal mechanical systems.

3:00pm **VT+MN-TuA3 A Rigorous Approach to Effluent Gas Management for the Vacuum Processing Industry**, ***Paul Dozoretz***, MKS Instruments, Inc. **INVITED**

Vacuum processing is consistently gaining momentum in the manufacturing of novel materials relying on thin film coating and implantation technologies. The vacuum systems developed for such new applications borrow from many of the standard vacuum processing techniques but consistently push the design limits in terms of the amount of precursor gas consumption and by-product mass generation. In order to handle the large amounts of effluent produced in some of these these processes it has become essential to better understand gas dynamics for the effluent flowing out of the chamber and into the pumping systems. In most cases, effluent gas must be captured or trapped before it can reach and irreversibly damage the pumps and before it can become a danger for the personnel operating the vacuum manufacturing tools. With the aid of gas dynamic modeling software, our engineering team has been able to better understand flow through effluent lines and develop more efficient gas trapping solutions for very novel applications spanning from the semiconductor to the aeronautical industries. In this presentation we describe the rigorous methodology used to guide and validate the design effluent gas handling systems. Detailed understanding of process chemistries and effluent physicochemical properties, combined with gas dynamic flow modeling, has revolutionized the way our team approaches effluent gas management and improved the speed at which customer effluent needs can be addressed.

4:20pm **VT+MN-TuA7 Compatibility of NEG Pumps with Particle-sensitive Applications: A Review of Recent Experimental Evidences**, *P. Manini, E. Maccallini,* ***Marco Urbano***, *M. Mura, T. Porcelli, F. Siviero*, SAES Getters, Italy

Non Evaporable Getter (NEG) pumps are frequently used when large pumping speeds for $H_2$ and active gases (i.e., $H_2O$, $O_2$, CO, $CO_2$) are required in conjunction with very small weight and size, reduced magnetic interference and vibration, or negligible power consumption. Thanks to these qualities NEG pumps are widespread in basic and applied research, such as particle accelerators, storage rings, synchrotrons and physics projects to achieve UHV or XHV conditions. Moreover, their use is becoming familiar in UHV analytical instrumentation such as SEM, TEM, surface science as well as portable mass spectrometry and transportation vacuum boxes.

In spite of the excellent results in terms of pressure ($10^{-11}$ mbar are currently achieved in many machines and values lower than $10^{-12}$ mbar have been measured in various experiments using NEG pumps), application in cryogenic superconductive radio frequency (SRF) cavities and other particle sensitive systems is not common so far. As a matter of fact, the use of NEG pumps is limited as a precaution against potential dust emission, which can be transported inside the vacuum envelope and may interfere with the electromagnetic fields and promote unwanted quenching phenomena.

Nevertheless, these systems could greatly benefit from the high pumping speed and compactness of NEG pumps, so that an assessment of the actual risk of dust release is gradually being undertaken by different players, including potential users in the accelerator community. Here we present and compare experimental data on particle emission collected with several techniques both on compressed and sintered NEG elements, discussing the differences. In particular, a class of sintered getters based on the ZAO® alloy proved to have extremely low particle emission, as shown by tests carried out in actual SRF cavities, where no measurable particle contamination as well as detrimental effect on the cavity efficiency and performances was observed.

4:40pm **VT+MN-TuA8 NEG Coated Chambers for XHV**, ***Marcy Stutzman***, *P.A. Adderley, M. Poelker*, Thomas Jefferson National Accelerator Facility

Non-evaporable getter (NEG) thin films are typically applied to uniform diameter tubes, such as used for accelerator beamlines. We have been extending the successful application of NEG coating to larger diameter and non-uniform chambers, such as the 36 and 41 cm diameter chambers for the Jefferson Lab polarized electron source, as well as atom trap chambers for MIT and JILA. We show that by combining the NEG coating with a small ion pump to handle the non-reactive gasses, the chamber can reach the low $10^{-12}$ Torr range, and adding additional NEG pumping yields extreme high vacuum (XHV), with measured pressure below $8x10^{-13}$ Torr. With this demonstration of a reliable and reproducible method to achieve room temperature XHV, we hope to demonstrate the benefits of NEG coated chambers beyond accelerator physics applications to other fields of physics and materials research.

5:00pm **VT+MN-TuA9 Ion Pump Noble Gas Stability Mechanism of Titanium Cathode Material**, ***Anthony Wynohrad***, Gamma Vacuum

It has long been established that ion pumps with titanium cathodes cannot pump large quantities of noble gases without releasing them back into the vacuum environment. Argon is the typical gas chosen for study of this phenomenon due to its prevalence in atmospheric composition and tendency for use in vacuum depth profiling applications. Traditional resolutions to Ar release is through the addition of denser cathode material (Tantalum) or titanium cathode architecture manipulation (triode). Various reports have shown the long term Ar stability of these methods to be subject to manufacturer claims.

To resolve reported discrepancies of Ar stability in ion pumps with titanium and tantalum cathodes, a detailed study of titanium with various physical attributes was conducted. Five different titanium/titanium alloys were tested for Ar instability at standard depth profiling pressures rather than accelerated high pressure testing. The conclusion was reached that varying the physical properties of the titanium can cause ion pumps to become Ar stable or Ar instable. Additionally, the time to reach instability is directly in correlation to the physical attributes of titanium.

5:20pm **VT+MN-TuA10 Ricor's MicroStar/Nanostar Compact Water Vapor Cryopump: Applications and Model Overview**, ***Rodney Harris***, Ricor-USA, Inc., *I. Nachman, T. Tauber, M. Kootzenko, B. Barak, E. Aminov, D. Gover*, RICOR Cryogenic & Vacuum Systems, Israel

Ricor Systems has developed a compact, single stage cryopump that fills the gap where GM and other type cryopumps can't fit in. Stirling cycle technology is highly efficient and is the primary cryogenic technology for use in IR, SWIR, HOT FPA, and other IR detector technology in military, security, and aerospace applications.

Current GM based dual stage cryopumps have been the legacy type water vapor pumping system for more than 50 years. However, the typically large cryopanel head, compressor footprint, and power requirements make them not cost and use effective for small, tabletop evaporation / sputtering systems, portable analysis systems, load locks, and other systems requiring small volume vacuum creation from medium, high, and UHV levels. The compact NanoStar configuration was designed specifically to address this vacuum chamber size area.

This single stage cryopump works well in-line with diffusion and molecular turbopumps. Studies have shown effective cooperation with non-evaporable getter technology as well for UHV levels.

Further testing in this area are ongoing. Temperatures created by Stirling cycle cryogenic coolers develop a useful temperature range of 40 to 150K.

Temperatures of approximately 100 K are sufficient to condense water and all hydrocarbons oil vapors. The wide temperature range can freeze out many other gaseous compounds.

## Actinides and Rare Earths Focus Topic
## Room: Central Hall - Session AC-TuP

### Actinide and Rare Earth Poster Session

**AC-TuP2 Sputter-Deposited Layers for Solid Phase Microextraction**, ***Tuhin Roychowdhury****, D. Patel, M.R. Linford*, Brigham Young University

Solid phase microextraction (SPME) is an effective analyte sampling method. It works by placing a coated fiber above a sample (headspace mode) or immersing it in a liquid sample such that molecules (analytes) of interest can be selectively captured and concentrated. The extracted species are then released into a chromatograph for separation, identification, and quantification. It is a 'green' method as no additional solvent is required in this process. Recently, we have developed a new class of SPME fibers that offer extraordinary capacity, sensitivity, and speed. They are prepared by sputtering a material under conditions that lead to a robust nanoporous coating on the fiber. In particular, silicon sputtering generates a porous surface that can be additionally oxidized, leading to a high density of silanol groups than can be subsequently silanized or used in other depositions. The surfaces and materials generated for SPME in this project have been characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), spectroscopic ellipsometry (SE), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and wetting. They confirm the synthesis of highly porous, hydrophobic materials. The performance of our 2 micron sputtered coatings has been compared to that of thicker (7 micron) commercial coating. Our fiber consistently outperforms the commercial fiber, showing significantly higher capacity, for example, for high molecular weight polycyclic aromatic hydrocarbons (PAHs). PAHs are a significant environmental pollutant. (They are produced from industrial wastes, incomplete combustion of fossil fuels, and natural emissions, and are detrimental to human health and the environment due to their carcinogenicity.) Hence, there is a need to identify these toxic pollutants. Real world samples, e.g., hops have also been analyzed. Different sputter coating thicknesses have been prepared and evaluated.

**AC-TuP3 Mechanical Behavior Improvement of Coated Epoxy Resins Exposed To Environmental Effects**, ***Dorina Mihut****, A. Afshar, S. Hill,* Mercer University*, G. Negrea,* Technical University Cluj Napoca, Romania*, R. Alyamani, A. Aldhubaie*, Mercer University

**Abstract**:

Epoxy resins based materials are widely used as a matrix component for marine, aviation, transportation and civil infrastructures as they are light weight and are offering high strength and stiffness-to-weight ratio as well as good corrosion resistance. However, during their usage these materials are exposed to exterior environmental effects which can significantly degrade their mechanical properties and preclude their prolonged use. The present research investigates the influence of metallic and ceramic coatings in order to enhance the mechanical behavior of the epoxy resin based substrate materials to a combination of exterior factors: ultraviolet (UV) radiation, moisture and erosion. The metallic and ceramic coatings were deposited using high vacuum DC magnetron sputtering equipment. The pristine and coated polymer based samples were further exposed to continuous and cyclic UV radiation and moisture (ASTM G 154 standard). The samples' morphology was characterized using optical microscopy and X-ray diffraction analysis was used for determining the chemical composition of the coatings. The mechanical properties of all samples were tested using the standardized three points bending test and their erosion behavior was also tested using an erosion tester.

## Biomaterial Interfaces Division
## Room: Central Hall - Session BI-TuP

### Biomaterial Interfaces Poster Session with Flash presentations

**BI-TuP1 Optimizing Micropost Arrays to Break Up Biofilms**, ***James Waters****, A.C. Balazs*, University of Pittsburgh

Surfaces covered with periodic arrays of microposts represent an appealing avenue of fouling mitigation, as they rely on a physical mechanism without unintended environmental consequences. In addition to reducing the area for contaminant cells to bind to the surface, the flow field generated by specific configurations of posts under shear may help push particles away from the surface, or break up biofilms as they form. We represent such a system computationally using a hybrid of bulk fluid simulated via the lattice Boltzmann method, and deformable vesicles, representing cells, simulated via that lattice spring method. This simulation methodology allows us to rapidly implement and test different surface structures, and explore how the parameters of post shape and arrangement can most effectively deter the accumulation of biofilms.

**BI-TuP2 Dynamic Field Testing of Fouling Release Coatings by a Rotating Disk System**, ***Julian Koc****, K.A. Nolte,* Ruhr-University Bochum, Germany*, A. Stephens,* Florida Institute of Technology*, M.P. Schultz,* United States Naval Academy*, G. Swain, K. Hunsucker*, Florida Institute of Technology*, A. Rosenhahn*, Ruhr-University Bochum, Germany

The development of materials with the capability to resist the accumulation of biomass on surfaces in contact with seawater (marine fouling) is both, economically and ecologically desired. To rank the performance of novel coating technologies, different lab and field screening methods have been established. While technical coatings are tested over several months, methods for short-term testing of thin film chemistries are missing. We developed a setup for dynamic, short term field testing of coatings. To obtain a constant shear stress during colonization, a rotating disc was used. The rotating disc was designed to be easily transported and installed at various marine testing sites. The shear situation above the disk was theoretically simulated and adjusted to shear ranges identified in recent laboratory experiments to be suited to distinguish the fouling-release potential of surfaces [1]. To validate the setup, self-assembled monolayers with well characterized physicochemical properties were tested under similar shear conditions, as in our recently reported laminar flow lab assay. The same discriminations with the same trends as in the lab assay were obtained for a mixed population of marine diatoms in the ocean. In the future, the setup will be used to compare the results of lab tests of new promising coating chemistries with short term dynamic field exposure.

[1] K. Nolte, J. Schwarze, A. Rosenhahn, *Biofouling* **2017**, in press

**BI-TuP3 Bioinspired Vascularized Polymers for Controlled Drug Delivery**, ***Kayla Marquis****, A. Webber, C. Howell*, University of Maine

Nearly all methods that deliver bioactive compounds to the surface of a substrate rely on application from above or fail over time due to depletion of compounds. Here we explore the use of natural vascular channels embedded within polymeric matrices to allow for continuous, targeted, low concentration delivery of bioactive compounds to the surface from below. To achieve this, networks of empty 3D printed vascular channels are continuously filled with bioactive compounds. The compounds flow through the vascular network and diffuse through the polymer, eventually reaching the substrate surface of the matrix. By varying the locations and depths of these vascular channels we demonstrate that the amount of material and duration over which it is delivered to the surface can be controlled. The ability to control the diffusion of compounds both spatially and temporally is key in developing assays that test the effects of chemical gradients on various systems at both the cellular and organismal levels. This approach may prove useful in applications such as toxicity and wound healing assessment and targeted antifouling surfaces.

**BI-TuP4 Measuring the Mechanical Properties of Hydrophobic Anti-Fouling Surfaces**, ***Samantha Zanetti****, S. Moorzitz, G. Dickinson, M. Figueroa*, The College of New Jersey

Biofouling by marine organisms causes damage to ships and underwater structures. Some anti-fouling coatings reduce adhesion by small marine organisms but are not as effective in deterring adhesion from barnacles. To develop a surface capable of further reducing barnacle adhesion, it is important to understand the chemical and mechanical interactions in the formation of bonds between the glue and surface. While some experiments have studied the mechanical properties of the cyprids and barnacles, their adhesion is complex and still not fully understood. Furthermore, there are only a few studies that have measured the adhesive properties of reattached barnacles. To study the adhesive properties of the glue, adult barnacles were removed from hydrophobic surfaces and the glue residue was characterized by atomic force microscopy (AFM).

Assessments were conducted on methylated and fluorinated self-assembled monolayer substrates. Substrates were prepared on glass slides that were cleaned with Piranha solution prior to use. Barnacles were reattached to the substrates in artificial seawater for two weeks. They were then removed via shear force following ASTM D5618-94. Separately, a mechanical testing frame was used to remove another set of reattached barnacles in a controlled manner. Force required to displace the barnacle was recorded and compared to the ASTM standard.

To determine the glue's viscoelastic properties and Young's Modulus, an AFM was used to collect force curves and images of the barnacle glue residue. The mechanical properties of the glue were recorded for each type of coating following an indentation procedure using an intermittent contact mode. Adhesion data and the deflection of the tip was used to plot applied force vs. vertical displacement. A contact model was applied to the approach and retraction curves to gather the viscoelastic properties of the samples.

The poster will present summer 2017 research results. This will include the measured mechanical properties of glue from reattached barnacles, retrieved from the AFM analysis and mechanical test strain data.

### BI-TuP5 *In Vitro* Degradation Performance and Increased Biological Response of a Surface Modified Mg-Al-Zn Alloy

*Michael Melia, D.C. Florian, J.R. Scully, J.M. Fitz-Gerald*, University of Virginia

As a lightweight metal with mechanical properties similar to natural bone, Mg and its alloys are great prospects for biodegradable, load bearing implants. However, the United States has yet to clear Mg for any substantial role in the body due to the concerns of electrochemically derived hydrogen gas and unpredictable loss of structural integrity as a result of a dynamic corrosion resistance varying with time. This research investigates how the chemical homogenizing effects of laser processing and the application of a corrosion resistant coating impacts the corrosion resistance, cell viability, and cell adhesion of the AZ31B (3 wt. % Al, 1 wt. % Zn, 0.3 wt. % Mn, and 95.7 wt% Mg) alloy in a physiological solution.

Cell viability and adherence measurements were carried out utilizing the osteosarcoma (MG63) cell line and were plated on the AZ31B specimens in the as-received, laser processed, and coated conditions. In vitro cell viability assays show improved cytocompatibility for both the laser processed and coated specimens over the as-received AZ31B alloy. The coated specimen performed the best with a 5 fold improvement in cell viability over the as-received alloy. Cell adhesion was further investigated by fixation of the MG63 cells and imaging using scanning electron microscopy (SEM). Electron micrographs revealed significant adhesion of cells to the coated specimen with limited adhesion for specimen in the as-received and laser processed condition.

Laser processing utilized a KrF pulsed excimer laser ($\lambda = 248$ nm and FWHM = 25 ns) which has been shown to reduce the corrosion rate of Mg alloys by an order of magnitude in NaCl containing solutions. Corrosion experimentation was performed under full immersion in a minimal essential media (MEM). Time dependent corrosion rates and electrochemical kinetics were analyzed using open circuit potential, electrochemical impedance spectroscopy, and potentiodynamic polarization measurements. The corrosion product morphology was investigated using SEM, energy dispersive spectroscopy, and x-ray diffraction. The coated specimens exhibited an order of magnitude reduction in cathodic kinetics after 24 hours of immersion in MEM compared to the as-received AZ31B alloy. The laser processed condition exhibited a 5 fold reduction in cathodic kinetics to the as-received alloy as well as maintaining an open circuit potential 150 mV lower than the coated and as-received specimen. The passivate nature of all three specimen conditions was similar.

### BI-TuP6 Interactions between Single Molecules and Surfaces

*C. Klinger,* TU Bergakademie Freiberg, Germany, ***Laila Moreno-Ostertag***, MPI for Iron Research, Germany, *C. Weber, P. Schiller, M. Valtiner*, TU Bergakademie Freiberg, Germany

Unraveling the complexity of the macroscopic world relies on understanding single molecule interactions and their scaling towards integral interactions at the meso- and macroscopic scale [1]. Here, I will discuss how one can measure the interaction free energy of single interacting functional groups at various solid/liquid interfaces. The adhesion between single molecules and surfaces in electrolytes is a central point regarding many biological systems and the delamination of coatings.

Single molecule force spectroscopy with an AFM is a suitable tool for measuring the work and force needed to unbind single molecules. The relation between the work of non-equilibrium trajectories and the free energy of interaction can be described by Jarzynskis equation [2]. So the surface-to-molecule bond rupture can in principle be characterized fully, but systematic errors arises. First, we will discuss how the effect of contour length of typically utilized molecular linkers such as PEG potentially adds a systematic bias on the free energy determined from AFM experiments. Secondly, also experiments with varying speed of the force runs were realized and the bias due to increasing rates (i.e. further shift from the equilibrium situation), which will be discussed in this contribution.

Finally, we will discuss in detail how single molecule unbinding energy landscapes can be utilized to predict scenarios where a large number of molecules simultaneously interact, giving rise to adhesive failure under corrosive and wet conditions. As such, our experimental strategy provides a unique framework for the molecular design of novel functional coatings through predicting of large-scale properties such as adhesion and molecular interactions in various systems based on experimentally determined single molecule energy landscapes.

[1] T. Utzig, S. Raman, and M. Valtiner, Langmuir 31, 2722-2729 (2015)

[2] S. Raman, T. Utzig, T. Baimpos, B. R. Shrestha, and M. Valtiner, Nat. Commun. 5, 5539 (2014)

### BI-TuP7 Proton Transfers Involved in Melanin Biosynthesis: Binding of Cysteine to Dopaquinone Investigated by Density Functional Theory based Calculation

***Ryo Kishida***, Osaka University, Japan

Melanin is a natural pigment present in many types of living organisms. The color of the skin, hair, and eyes is a manifestation of melanin biosynthesis (melanogenesis). Melanogenesis is initiated by oxidation of tyrosine to form reactive dopaquinones. The formed dopaquionone rapidly reacts with cellular cysteine, resulting in the generation of yellow to reddish brown pheomelanin. At lower concentration of cysteine, dopaquionone undergoes intramolecular cyclization, resulting in the generation of brown to black eumelanin. Thus, the reactions of dopaquinone (cyclization and cysteine binding) affect the pheomelanin/eumelanin ratio, determining the body color. The color of eumelanin is further controlled by its monomer ratio. Eumelanin monomers are formed from dopachrome, which is a molecule generated after the stage of dopaquinone.

We have investigated the reactions of dopaquinone and dopachrome [1-4]. In this symposium, we present our recent mechanistic study on reactions of dopaquinone with a focus on the cysteine binding. Using density functional theory based calculation, we computed the energy profiles for the approaching of cysteine to dopaquinone and obtained stable cysteine-bound structures. We found that the cysteine-bound structures can undergo intramolecular proton transfer for further stabilization with fairly small activation energy.

[1] R. Kishida et al., Pigment Cell Melanoma Res. 27 (2014) 734.

[2] R. Kishida et al., Biochim. Biophys. Acta 1850 (2015) 281.

[3] R. Kishida et al., J. Electron. Mater. (2017) doi:10.1007/s11664-017-5299-x.

[4] R. Kishida et al., Biochim. Biophys. Acta (to be submitted).

### BI-TuP10 Interferometry: A New Way to Study Corrosion at Confined Interfaces

***Claudia Merola**, H.-W. Cheng,* Max Planck Institute for Iron Research, Germany, *M. Valtiner,* University of Freiberg, Germany

Understanding marine corrosion and biofouling is of central importance for designing materials for marine use that last longer and protect more effectively from biofouling. Many different types of destructive attack can occur to structures, ships and other equipment used in sea water service.

Crevice corrosion (CC), which is corrosion at an interface, still remains one of the most difficult types of corrosion to detect and to prevent. Most often CC occurs in narrow fissures where oxygen access is poor and a stagnant electrolyte solution is present. Experimentally it is a challenge to obtain in-situ information of processes in confined geometries and to establish well defined confined situations in the first place.

Here, we show how white light interferometry[1] can be utilized, for the first time, to study and monitor in situ the initial stages of the crevice corrosion process of thin layers of different metals[2] (e.g. Ni, Al, Au..) in different concentrations of NaCl solutions. Using Mica as a crevice former in an electrochemical surface apparatus allowed us to provide a deeper understanding of the initiation of the corrosion process, which also occurs at the adhesive interface of bio organism such as barnacles or mussels.

Our new approach provides a real-time view of the initial corrosion of confined surfaces, and hence may contribute to a deeper general understanding, and ultimately prevention, of localized corrosion and corrosion underneath biofoulers.

[1]J. Israelachvili *et al.*, Recent advances in the surface forces apparatus (SFA) technique. *Reports on Progress in Physics* **73**, 036601 (2010).

[2] B. R. Shrestha *et al.*, Real-Time Monitoring of Aluminum Crevice Corrosion and Its Inhibition by Vanadates with Multiple Beam Interferometry in a Surface Forces Apparatus. *Journal of the Electrochemical Society* **162**, C327 (2015, 2015).

### BI-TuP11 Stimuli-responsive Thin Films made from the Mucilage of *Opuntia Ficus-indica* Cactus

***Zeinab Veisi***, University of South Florida, *M. Cardenas, A. Cardenas-Valencia*, SRI International, *R. Toomey, N. Alcantar*, University of South Florida

We have used the mucilage of *Opuntia ficus-indica* cactus to fabricate ultra-thin films of surface-attached networks. The gelling properties and swelling behavior of these thin films were studied as a function of various stimuli to determine the main factors affecting the responsiveness of such layers.

*Opuntia ficus-indica* belongs to the cactaceae family, and is grown in dry regions. Its abundance makes it a promising commercial source of industrial pectin. Mucilage extracted from *Opuntia ficus-indica* is a heteropolysaccharide composed of a backbone chain structure of α-D-galacturonic acid and β-L-rhamnose interrupted by different neutral sugars. The carboxyl groups present in a polygalacturonic acid chain can be cross-linked in the presence of divalent ions to render hydrogel networks with conformations responsive to internal and external variables. The presence of a considerable amount of water within the polysaccharide matrices renders unique hydrophilic gels suitable to be used in a wide range of applications.

Thin films of surface-attached polysaccharide networks were fabricated by spin-casting solutions of mucilage. $Ca^{2+}$ ions were then introduced to obtain cross-linked networks with adjustable extent of crosslinking. The fabricated surface-attached thin films of cross-linked polysaccharide were then characterized by Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) Spectroscopy and ellipsometry. Swelling behavior of the confined surfaces was studied as a function of temperature in contact with aqueous solutions, and their response was perturbed by different stimuli. Moreover, surface-attached networks were exposed to buffer solutions of pH of 9 and 2 to investigate the effect of charge concentrations on the response of networks.

The average water content in the networks as a function of temperature and the extent of crosslinking was precisely measured using ellipsometry. The results revealed that the extent of equilibrium water content and release profiles of thin films strongly depend on the degree of crosslinking. Moreover, the extent of equilibrium water uptake is affected by the values of pH of the media.

Our findings provide an improved understanding of the chemical properties, functionalities and the gelling behavior of thin films of surface-attached naturally occurring polysaccharides which can be employed for establishing responsive surfaces with tunable response suitable for the pharmaceutical and biotechnology industries.

### BI-TuP13 Effect of Topography on Retinal Stem Cell Viability and Regrowth, *Aleksandr Filippov*, *Y. Tian, Y. Xie*, SUNY Polytechnic Institute

Age-related macular degeneration is a devastation eye condition that inflicts damage to the retina and leads to irreversible vision loss. The retina is made up of several layers of light-sensing cells, which are supported and nourished by the retinal pigmented epithelial (RPE) layer. The RPE cells sit atop the Bruch's Membrane and form a highly-selective blood-retinal-barrier that is critical for retinal homeostasis. In this project, we attempt to recreate the barrier in vitro using elestrospun nanofibers. Human RPE cells were cultured on nanofibers made from natural and synthetic polymers, such as chitosan and polycaprolactone, with Synthemax and gelatin as controls. We found that human RPE cells demonstrated proper morphology and protein expression when cultured on the chitosan substrate.

### BI-TuP14 DNA Interactions with Elastin like Polypeptide Coacervates, *Telmo Díez*, *P.A.H. Nguyen, N. Carroll, J. Satterfield, G.P. Lopez,* University of New Mexico

Intrinsically disordered proteins (IDPs) are dynamic biomaterials used by mammalian cells in cell signaling, transcription, and chromatin remodeling functions. In native cells, they are frequently used in packaging and un-packaging of nucleic acids (NAs), making them promising biomaterials for drug delivery and gene delivery. Elastin Like Polypeptides (ELPs) are synthetic biopolymers that have similar structural features to natural IDPs with many similar associated functions. In this research, we focus on replicating IDPs' ability to assemble into hierarchal phase-separated granular structures and interact with nucleic acids using cationic ELPs. Importantly, ELPs condense to form coacervates above a lower critical solution temperature (LCST). Below this temperature, ELPs exist as a fully soluble random coil polymer. In this study, we use an ELP comprising 8 positive charges due the presence of 8 lysines interspersed within the chain. We demonstrate that condensed ELP coacervates provide the necessary charge density to attract and encapsulate nucleic acids. Here, ELP coacervates are incubated with fluorescently labeled DNA containing a Cy3 fluorophore on its 5' end. We characterize the amount of DNA captured by fluorescence intensity measurements that are taken prior to and following formation of a phase-separated ELP coacervate in aqueous solution. Furthermore, we use microfluidics to form aqueous microdroplets comprising ELP and fluorescent DNA to visualize DNA capture within ELP coacervate spheres via fluorescence microscopy. ELP coacervates formed by heating the microdrops above the ELP transition temperature are shown to electrostatically complex with- and capture DNA. We characterize the thermodynamic binodal boundary (i.e. temperature-dependent phase boundary) of the ELP to resolve the ELP volume fraction within the coacervate to determine the optimal temperature to maximize DNA capture. These initial studies will inform our future work to engineer smart, programmable nanoparticles for the delivery of nucleic acids for gene therapy applications.

### BI-TuP15 Bovine Aortical Endothelial Cell Encapsulation with Elastin-like polypeptides (ELP) and bis(sulfosuccinimidyl)suberate (BS3)., *Phuong Anh Nguyen*, *T. Diez Perez, H.E. Canavan*, University of New Mexico, *N.J. Carroll*, Universiity of New Mexico

Chronic wounds do not adequately recover through the healing process and have become a major challenge to healthcare systems worldwide. In the U.S., chronic wounds affect an estimated 6 million people per year, costing more than $25 billion annually due to complications and over $18.5 billion in associated care. Current biomaterials for wound healing scaffolds including aglinate, hydrofibers, foam, hydrogels, cadaver skins, fetal cow skin, skin grafts or fish skin to wounds to encourage healing. However, common drawbacks include poor biocompatibility, risk of disease transmission and host rejection. Bioprinting of hydrogel materials has emerged as a flexible tool with potential to obviate these problems. For example, tissue engineering by extrusion bioprinting uses robotic deposition to print cells encapsulated in hydrogel scaffolds to form new organs or tissues. However, biocompatible and biofunctional materials for printable hydrogels are lacking. We propose to encapsulate cells in novel microgel materials, elastin-like-polypeptides (ELP), to create printable bioinks that are biocompatible, bioinert, and recapitulate physicochemical cues of natural extracellular matrices. In our study, ELP hydrogels are formed by crosslinking ELPs with bis(sulfosuccinimidyl)sulfate (BS3), an amine-reactive crosslinker, to encapsulate bovine aortic endothelial cells within the formed hydrogels. Initial testing via live/dead assays shows cells are able to survive in the hydrogel scaffold for many days. Hydrogel stiffness can easily be controlled via temperature, pH, and crosslinker concentrations. Future work leveraged from these assays will be encapsulation and differentiation of mesenchymal stem cells (MCMs) for programmable wound healing.

### BI-TuP16 Direct Electron Beam Imaging of Proteinaceous Fibrils, *T.M. Thieu*, KRISS, Republic of Korea, *T.H. Ha*, KRIBB, *SangJung Ahn*, KRISS, Korea, Republic of Korea

Direct electron beam imaging method was investigated with abnormal protein assembly of amyloid fibrils. Without and with metal coating, the fast electron beam methods such like scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to observe in nanoscale and compared with slow tip-probing method, atomic force microscope (AFM). As a model protein for amyloid fibril, insulin protein (15 kDa) was chosen, whose aggregation has been believed to have a relation with type II diabetes in human. The insulin amyloid fibrils have grown under several effector molecules such as treholose, ectoines, and citrulline in order to discriminate the morphology differences in various conditions. The direct imaging of proteinaceous fibrils with electron beam was possible only in narrow windows of imaging conditions due to the facilitation of electrostatic charging effect, which is dependent on the underlying substrate. The comparisons of images with electron beams and physical tip-contact were conducted and analyzed in terms of measurement speed, charging, and mechanical damages.

### BI-TuP17 Textured TNZT Foams for Bone Implant Applications, *Elizabeth Blackert*, *S. Murguia, M. Kramer, M. Young, S.M. Aouadi*, University of North Texas

TNZT alloys with compositions of Ti-35Nb-7Zr-5Ta are materials that are more biocompatible than the more widely used Ti-6Al-4V alloy since each of its constituent elements is biocompatible. In addition, it has the lowest Young's modulus of all the titanium-based alloys created so far (50-60 GPa). This property allows for a greater transfer of functional loads, which ultimately leads to bone growth stimulation. TNZT alloys were produced by arc melting of pure elements and were forged into rods. Oxide nano-scaffolds were grown on TNZT samples to investgate the potential of these nanostructures surfaces to improve osseointegration. These nanoscaffolds were grown using the hydrothermal method to create an oxide film. The alloys with and without nano-scaffolds were characterized using top-view and cross-sectional scanning electron microscopy equipped with an energy dispersive x-ray spetrometer to investigate the structure, morphology and chemistry of the resulting nanostructures. Finally, the formation of hydroxyapatitite on the modified surfaces was investigated upon immersion in simulated body fluid (SBF).

### BI-TuP18 Synthesis and Immobilization of Silver Nanoparticles in Natural Hydrogels by Directed Liquid-plasma Nanosynthesis, *Camilo Jaramillo*, *A.R. Shetty, A.F. Civantos, S.L. Arias, J.C. Devorkin,* University of Illinois at Urbana-Champaign, *S. Chang*, Nanjing University of Aeronautics and Astronautics, China, *J.P. Allain*, University of Illinois at Urbana-Champaign

Plasma technology has seen an increased demand in nanotechnology, because of the changes in chemistry and morphology it can induce. These capabilities enable novel applications in a wide range of areas from advanced optical components to biomaterials [1]. Traditional plasma-based techniques work in low-pressure controlled environments. Compared to vacuum-based systems, atmospheric-pressure plasma (APP) systems offer reduced costs (e.g. no vacuum needed), higher reaction rates due to their high neutral-particle component and low-temperature treatment of polymer-based materials [2]. In addition, for specialized applications such as biology or catalysis, APP can offer treatment under gaseous or aqueous environments. One weakness of APP is the difficulty in controlling the coupled ion-neutral species and in turn high-fidelity modification of materials. One alternative to APP is the ability to tailor surface properties by careful control of species in the liquid plasma-material interface resulting in manipulation of nanostructured surface properties. Directed liquid-plasma nano-synthesis (DLPNS) is used in this work as the basis for systematic studies on the synthesis of silver nanoparticles (Ag NPs) in aqueous solution with DLPNS compared to in-vacuum directed plasma nanosynthesis (DPNS) on natural hydrogel matrices. Silver NPs are important for antimicrobial applications due to their unique antibacterial properties [3], but they also possess cytotoxic properties, making them harmful to human tissues [4]. Chitosan (CS) is a biodegradable, biocompatible and non-toxic natural biopolymer, which has been studied due to its antimicrobial properties [5]. DLPNS was used to treat Ag and Ag/CS solutions, driving NPs synthesis and surface nanopatterning. Surface morphology and composition were studied with SEM and EDS, respectively. Ambient-pressure *in-situ* XPS was used to measure irradiation-induced chemistry changes of CS. The antimicrobial properties of synthesized Ag NPs and nanostructured CS was systematically studied with control parameters such as energy and fluence. Notable transformation of the hydrogels was achieved, with self-organized pillar structures and porous structures produced on CS.

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## Spectroscopic Ellipsometry Focus Topic
## Room: Central Hall - Session EL-TuP

## Spectroscopic Ellipsometry Poster Session

### EL-TuP1 Ultra High-speed Spectroscopic Ellipsometry and its Applications, ***Gai Chin***, ULVAC, Japan

As a comprehensive manufacturer of metrology tools and deposition tools, ULVAC developed an innovative ultra high-speed spectroscopic ellipsometer for many deposition applications, such as PVD, CVD, ALD and others.

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

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

This paper describes the principle, system configuration and our creative efforts on developing a series of ultra high-speed spectroscopic ellipsometers. Some of the novel applications will be also introduced, such as the PVD, CVD, ALD, EUV, OLED, MEMS and some measurement data of thin films from the semiconductor, flat panel display and other industries.

### EL-TuP2 Comparing and Evaluating the Calculation Results of Measurement Uncertainty for Various Types of Rotating-element Spectroscopic Ellipsometers, ***YongJai Cho***, *W. Chegal, H.M. Cho,* Korea Research Institute of Standards and Science, Republic of Korea

Various multi-channel rotating-element spectroscopic ellipsometers have excellent measurement abilities like real-time, high-precision, non-destructive, and contactless schemes, and as a result have been widely used in a semiconductor manufacturing process. With the development of semiconductor device process technologies, the thickness of the thin film used for these technologies is getting smaller and smaller and thus reaches a level of atomic layer and the shape of the nano pattern is changed from a two-dimensional structure into a three-dimensional structure and thus is becoming increasingly complicated. Therefore, for the rotating-element spectroscopic ellipsometers to be continuously used as a measurement tool for next-generation semiconductor industries, it is important to continuously enhance their measurement uncertainties. Recently, we developed the universal evaluations and expressions of measuring uncertainty for all types of rotating-element spectroscopic ellipsometers. We also introduced a general data-reduction process to represent the universal analytic functions of the combined standard uncertainties of the ellipsometric sample parameters. To solve the incompleteness of the analytic expressions, we formulated the estimated covariance for the Fourier coefficient means extracted from the radiant flux waveform using a new Fourier analysis. Our approach can be used for providing a method for calculating a theoretical model equation which may be applied to various kinds of multi-channel rotating-element spectroscopic ellipsometers and may determine a measurement confidence level thereof, that is, a theoretical equation on standard uncertainties of ellipsometric parameters determined on the basis of a series of observations for a sample. In this presentation, it will show that the calculation data of the combined standard uncertainty for the various types of the rotating-element spectroscopic ellipsometers are obtained using the universal expressions for the combined standard uncertainty. In particular, the calculation results for the dual-rotating-compensator spectroscopic ellipsometers will be compared and evaluated with the calculation results for the common single-rotating-element spectroscopic ellipsometers.

### EL-TuP3 Ellipsometry Analysis of a Germanium-on-insulator Wafer, ***Rigo Carrasco***, *N. Samarasingha Archichchege*, New Mexico State University, *B.Y. Nguyen,* Soitec, France, *S. Zollner*, New Mexico State University

Germanium based photonic devices attract a lot of interest due to the fact that its band structure is easily influenced by strain and alloying with tin. A direct bandgap group IV semiconductor will show an improvement in efficiency in optoelectronic devices. Utilizing a germanium-on-insulator (GOI) substrate is a key feature for future silicon compatible germanium based devices, allowing for easier integration by the microelectronics industry. [1]

Here, we analyzed the optical response of a GOI bonded wafer via spectroscopic ellipsometry. The ellipsometric angles, psi and Delta, and the depolarization were acquired from 0.5 to 6 eV in 0.01 eV increments using a J.A. Woollam variable angle spectroscopic ellipsometer (VASE) and from 0.1 to 0.8 eV using a Fourier transform infrared (FTIR) ellipsometer, allowing high precision measurements in the mid-infrared range. The measurements in both ranges were performed at angles of incidence from 60 to 75 degrees in 5 degree increments.

The optical response of the GOI wafer was modeled with four layers (Si, buried oxide, Ge, native oxide). As expected, strong interference oscillations were observed below the E1 critcal point of Ge. For Ge, we used the parametric semiconductor oscillator model and compared it to our previously determined optical constants of bulk germanium. We are particularly interested in differences near the direct band gap. The infrared phonon vibrations of the buried oxide were also visible in the measurements. The same measurement procedure was performed on the GOI wafer before and after cleaning the sample to observe the optical effects of a native surface oxide. While the pseudo-dielectric function of the GOI sample appeared different from that of a bulk Ge sample due to interference effects, the optical constants of the germanium layer only showed small differences. We did not find any differences in the electronic structure of bulk Ge and a thin bonded Ge layer.

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2016 Int. Conf. on Compound Semiconductor Manufacturing Technology, Miami, Fl, May 16-19, 2016

## MEMS and NEMS Group
## Room: Central Hall - Session MN-TuP

## MEMS/NEMS Poster Session

**MN-TuP1 Method for Patterning Crystal Colloidal Masks Using Poly (Acrylic Acid)**, ***Connor Smith****, *S.L. Burkett*, The University of Alabama

Nanosphere lithography is a nanopatterning technique which has been a useful method for creating nanoscale features, such as nanopillars, that are used in MEMS and NEMS devices. This is achieved by ordering nanospheres in close-packed crystal colloidal masks on a substrate and physically etching said substrate via the interstitial spaces between the nanospheres. Methods for ordering these nanospheres into crystal colloidal masks has been accomplished in many ways, with spin-coating being one of the most cost effective and simplest to implement. Unfortunately, only a few methods exist for patterning these crystal colloidal masks, and few utilize traditional optical lithography techniques. In this work, a method for patterning crystal colloidal masks that are formed via spin-coating is introduced. This method involves spin-coating nanospheres in a solution of water and poly (acrylic acid), and then using modified traditional optical lithography and plasma ashing techniques to pattern the resulting crystal colloidal mask. Once the mask is patterned, normal physical etching methods may be used to further pattern the substrate below the nanosphere embedded poly (acrylic acid) layer. With this new method, patterning crystal colloidal masks for use in nanosphere lithography should be easier due to the wide spread availability of traditional optical lithography tools and instruments.

**MN-TuP2 Understanding the Influence of Space Charge Region on Electrical Behavior of ( $Pb_{0.95}La_{0.05}$)($Zr_{0.54}Ti_{0.46}$)$O_3$ Thin Film Capacitors Designed using Top Electrodes of Different Various Work Functions**, ***Vaishali Batra§§§***, *S. Kotru, G.D. Cabot II, V.N. Harshan*, The University of Alabama

Ferroelectric lanthanum modified lead zirconate titanate (PLZT) material has excellent electronic and optical properties due to which it meets the requirements for various device applications such as optical modulators/transducers, MEMS and smart sensors. Recently this material is being explored for photovoltaic applications. To design devices, the material is integrated with conducting electrodes to prepare metal/ferroelectric/metal (MFM) heterostructures. Electrical behavior of the devices strongly depend on the properties of the electrode/s used to design the MFM structures. In this work, we investigated the dependence of electrical properties of metal/PLZT/Pt capacitors, on a variety of top electrodes, having different work functions (Au, Pt etc.) with Pt serving as bottom electrode.

Thin films of $Pb_{0.95}La_{0.05}Zr_{0.54}Ti_{0.46}O_3$ (PLZT) were fabricated on Pt(111)/Ti/$SiO_2$/Si(100) substrates by chemical solution deposition method. Various metal electrodes, with varying work functions, were deposited on top of these films to prepare metal/PLZT/Pt capacitors. The prepared MFM heterostructures form space charge regions at the interfaces between PLZT film and electrode material. Due to different top electrode used to design the capacitor structure, the top interface differs from each other. A detailed analysis of the polarization-electric field (P-E) curves, capacitance-voltage (C-V) characteristics, permittivity-frequency ($\varepsilon_r$-f), and current-voltage (I-V) measurements of each of the capacitors allowed us to understand the variation in electrical properties as a function of top electrodes. This variation is mainly attributed to the modification in metal/ferroelectric Schottky contact at the top interfaces which results in creation of different interface electric field, thus altering the properties of PLZT thin film capacitors. Results obtained from this study can guide us to choose the correct electrode material for designing capacitors for a particular application (photovoltaic devices or other types of sensors).

**MN-TuP3 Tribology and Locomotion of Untethered Scratch Drive Actuators with Applications to MEMS Microrobotics**, ***Ratul Majumdar***, University of Illinois at Chicago, *L. Stan, R. Divan,* Argonne National Laboratory, *I. Paprotny*, University of Illinois at Chicago

Untethered Scratch Drive Actuators (USDAs) [1] have been widely used for actuation of MEMS devices, for example the assembly of 3D MEMS structures [2] and as propulsion mechanisms for stress-engineered MEMS microrobots [1]. These electrostatic actuators show fast and reliable motion on a power delivery substrate along with the ability to provide forward force of 30μN [2]. The power delivery substrate of these USDAs consist of parallel set of interdigitated metal electrodes with a high-k dielectric layer deposited on top [1,3]. The metal electrodes consist of Cr/Au/Cr(10/50/10nm) layers of 2 μm spacing patterned by electron beam lithography. Sputtered yttria-stabilized zirconium oxide (YSZ) of 500μm thickness is used as the dielectric layer. The sputtering parameters, especially the deposition pressure, along with the gas flow of argon and oxygen play an important role in determining the dielectric constant and hence, the power transferred to the USDA for actuation. Variation in the deposition pressure can improve adhesion of the dielectric layer and reduce the delamination during USDA motion. Application of ac voltage between the two parallel set of electrodes results in coupling of capacitive force to the microrobot chassis, thus supplying power to backplate and bushing of the USDA for translation.

For straight motion, a waveform primitive (Fig. 1, supplemental file) with amplitude ranging from 0 to 200V and frequency (f) of 15Hz was applied to the substrate. The waveform is symmetric along horizontal X axis to prevent accumulation of charge on the substrate. The lowest ($V_{low}$) and highest ($V_{high}$) value of the voltage waveform is varied and the corresponding motion of the USDA is recorded. The cutoff point at which USDA shows actuation depends on the quality of the dielectric (Fig.2). Interesting interaction with the substrate during release stage is observed by analyzing the $V_{low}$ (Fig. 3 and 4). Improved efficiency of the substrate by transferring more power to the USDA is observed for the power delivery substrate with the YSZ grown at higher pressure (25mTorr). That results in reliable motion and less delamination of the dielectric surface.

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**MN-TuP5 Effect of Seeding Material on $Sc_{0.125}Al_{0.875}N$ c-axis Orientation**, ***Erica Douglas***, *M.D. Henry, T.R. Young, B. Griffin*, Sandia National Laboratories

While piezoelectric AlN is presently implemented into several commercial applications for electronic devices (such as bulk acoustic wave (BAW) and surface acoustic wave (SAW) filters), alloying AlN with Sc is actively being investigated as a method for increasing the piezoelectric coefficient $d_{33}$. $Sc_XAl_{1-X}N$, with x approaching 40%, has reported an increase in the piezoelectric coefficient of almost 4X, with potential for high impact for wireless applications by improving bandwidth and decreasing insertion loss. However, the addition of Sc into AlN has led to secondary grain growth, observed even for low Sc content thin films.

This work will demonstrate enhanced c-axis orientation of polycrystalline $Sc_{0.125}Al_{0.875}N$ on <100> silicon by reactive sputtering with various seeding material, including Si, Pt, and AlCu. We will characterize (100) secondary grain growth on Si as a function of film thickness, as well as X-ray diffraction rocking curve full width half maximum (FWHM) of the (002) orientation. As film thickness increases, rocking curve FWHM approach 1.3 degrees for a 2.1 um film; low FWHM values are known to have high piezoelectric coupling. In addition, c-axis orientation was investigated with metal seeding material such as Pt and AlCu. 750nm $Sc_{0.125}Al_{0.875}N$ exhibited a 20% reduction of (002) FWHM and complete suppression of (100) secondary grain growth when seeding on AlCu as compared to Si.

To quantify the effect of $Sc_{0.125}Al_{0.875}N$ growth, contour mode width extensional resonators (CMRs) were fabricated and tested to extract fundamental device parameters such as quality factor(Q) and effective piezoelectric coupling coefficient ($K_{eff}^2$). The method for suppression of (100) secondary grain growth and improved (002) FWHM utilizing AlCu is CMOS compatible and is shown to create CMRs with -4 dB insertion losses and $K_{eff}^2$values of 2.3%.

This project was supported by the LDRD program at Sandia National Laboratories. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. The authors acknowledge and thank the staff of Sandia's MESA fabrication facility.

**MN-TuP8 MEMS-Based, High-Resolution Nanocalorimeter for Characterizing Phase Transitions in Samples in the Sub-Microgram Range**, ***Zhu Diao***, Stockholm University / Halmstad University, Sweden, *D. Campanini, A. Rydh*, Stockholm University, Sweden

High quality thermodynamic measurements are among the essential tools to investigate fundamental properties of materials. Novel materials are often only available in minute amount when first synthesised. Hence, it is of paramount importance to develop thermodynamic measurement techniques for small-sized samples. However, studies involving samples of sub-μg in masses are extremely difficult to perform. Conventional calorimeters are marked by the large heat capacity of the calorimeter cell (addenda), thus, not suitable for measuring sub-μg samples. Rapid development in the MEMS

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*** MEMS/NEMS Best Paper Award Finalist**

industry has led to the creation of nanocalorimeters [1]. Typically, these devices are constructed on bulk micromachined membranes, whose contribution to the device addenda is vanishingly small.

We have developed a MEMS-based, truly differential nanocalorimetry platform, which is capable of performing specific heat measurements on sub-μg of high-quality, single crystalline samples in a wide temperature range between 0.3 K – 400 K [2,3]. It operates according to a refined ac steady-state method, leading to both ultrahigh resolution (better than several in $10^{-5}$) and superior absolute accuracy (1 – 2%) [2]. The calorimeter consists of two 150-nm-thick $SiN_x$ windows, one serving as the sample cell while the other being the reference cell. Each calorimeter cell contains a GeAu thermometer, a titanium ac heater, and an offset heater. The annealed GeAu thermometer shows an almost temperature-independent relative sensitivity $|d\ln R/d\ln T| \sim 1$, covering the whole temperature span of interest.

We demonstrate the capability of our nanocalorimeter through measurements of high purity gallium samples with masses in the range of several hundred nanograms to a few micrograms. α-Ga, the stable polymorph of solid gallium, melts at 302.9 K. Upon cooling, significant supercooling occurs and it may solidify into the metastable β-phase. Compared with α-Ga, β-Ga retains significantly enhanced electron-phonon coupling, leading to an elevated superconducting transition temperature above 6 K. We show that the melting and solidification transition of gallium can be monitored in-situ on our nanocalorimeter utilizing the offset heater, and present specific heat data of both phases across the full temperature range. The high-resolution of our calorimetry scheme also allows in-depth characterization of the superconducting transition of β-Ga and the deduction of a number of important superconducting parameters.

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**MN-TuP9 PLD covering the Innovation Chain to Accelerate the Commercial Uptake of Novel Thin Film Materials**, ***Matthijn Dekkers***, *J.A. Janssens*, Solmates, Netherlands

It is well known that Pulsed Laser Deposition (PLD) is a very flexible and versatile technique allowing fast optimization of new and complex material thin films. The unique features of PLD allow for the integration of “Beyond Moore” materials in CMOS and new devices. However, mainly because of the sample size, the developed materials and processes in PLD research tools only just make it into demonstrator devices. In order to make it into commercial applications, next generation PLD equipment is needed to bridge the gap between demonstrator and the prototype – pilot – production stages.

The Solmates PLD platform is the next step beyond fundamental PLD research. The reliable hardware is flexible for fast process optimization and allows uniform thin film deposition up to 200 mm diameter with high reproducibility. The automated software ensures easy operation and stable performance. These characteristics enable the integration of PLD thin films in applications for (pilot) production and commercialization.

In this contribution the latest performance and specifications of Solmates PLD platform are addressed. Data on stability and reproducibility of wafer scale deposition of PZT thin films with excellent properties will be presented. Furthermore, two qualified processes Indium Tin Oxide and Aluminum Oxide thin films will be used to show some key capabilities of PLD such as damage free deposition on organic electronics or control of thin films density and microstructure for optical or sensing applications.

## Plasma Science and Technology Division
## Room: Central Hall - Session PS-TuP

## Plasma Science and Technology Poster Session

**PS-TuP1 Particle Kinetic Simulation of Low-temperature Low-pressure HiPIMS Plasma**, *N.T. Lauer*, ***Natale Ianno***, University of Nebraska-Lincoln

Leveraging the advantages of high impulse magnetron sputtering (HiPIMS) requires knowledge of the temporal evolution characteristics and transport properties of the target material from the cathode to the substrate. These are difficult characteristics to measure directly. Determining the desired process parameters required for specific results by experiment, such as pulse voltage, duty cycle, pressure, magnetic field strength and profile, electrode separation, substrate biasing, and target current density, is time consuming and expensive involving multiple experiments combined with months of characterizing depositions. Also, this approach must be repeated for each target material and gas mixture used. This makes the ability to model and predict plasma properties and deposition or etching results due to external driving parameters via computer simulation attractive.

A *1d3v* particle-in-cell (PIC) *local density adjustment* Monte-Carlo-Collision (LDA-MCC) model has been applied to model the specifics of sputtering using HiPIMS. Physics of the plasma-target interaction and diagnostics were incorporated into the model resulting in the ability to better understand the target species evolution at the cathode and subsequent transport to the substrate. The LDA-MCC was used regarding specific collision types to support transient particle volume density gradients and population inversions in the plasma associated with HiPIMS. Temporal evolution of species energy distribution functions (EDFs), volume densities, and populations at various locations within the plasma are characterized. Simulation predictions are compared with a variety of different experimental results in the literature supporting the validity of the model. These results will support future enhancements to the model to explore substrate bias effects on the process of target ion transport, tailoring energy distributions of deposited ions at the anode, investigating the utility of synchronized pulsed substrate biasing, and their effects on deposition characteristics.

**PS-TuP2 QDB: the Quantemol Database of Plasma Processes**, *C. Hill, S. Rahimi, D.B. Brown*, ***Anna Dzarasova***, *J.R. Hamilton, S. Zand-Lashani*, Quantemol LTD, UK, *J. Tennyson*, University College London, UK

QDB (https://quantemoldb.com)[1] is a database of plasma reactions and chemistries which is being expanded to include surface interactions and processes occurring at interfaces. This database aims to become a basis for computational model development for plasma-assisted processes. Such processes have become more and more popular, and increasingly allow better control and achieve high precision[2]. A way to reduce development risks in plasma chamber design and process optimisation is modelling the plasma kinetics and better understanding plasma-surface interactions. This, in turn, requires an understanding of processes using atomic-scale physics and where scaling becomes non-linear.

The QDB web software provides a platform for users to download, upload, compare and validate data, and exposes an Application Programming Interface (API) for its automated retrieval in a range of formats suitable for use in modelling software. The software was used to deposit industrial plasma chemistries developed within Powerbase project to be accessed via the API using specifically. Experimental validation was provided by industrial partners of Powerbase project. The library of chemistries and examples and datasets has been further developed with both experimental and theoretical sources by Quantemol staff and by our community of users.

In this presentation we will describe recent Powerbase developments in QDB, with a focus on the increased provision of data relating to the interaction of particles with surfaces. This has required the expansion of the QDB data model to include a characterization of the surface (substrate) composition and structure as well as the description of the behaviour of individual adsorbed species (desorption energy, diffusion energy, etc.)

It is hoped that the database and its associated online web application software and API will prove useful to the AVS community, particularly in commercial and academic research areas related to modelling plasma-enhanced processes.

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Acknowledgment: this project has received funding from the Electronic Component Systems for European Leadership Joint Undertaking under grant agreement No 662133. This Joint Undertaking receives support from the European Union’s Horizon 2020 research and innovation programme and Austria, Belgium, Germany, Italy, Netherlands, Norway, Slovakia, Spain, United Kingdom.

**PS-TuP3 Self-neutralized Ion Beam by Pulsed Plasma with Synchronous Afterglow Bias**, ***Ya-Ming Chen***, *R. Sawadichai, V.M. Donnelly, D.J. Economou*, University of Houston

Precise control of the ion flux and ion energy distribution (IED) is crucial for advanced plasma processes that require high selectivity and minimum substrate damage. To neutralize the space charge of the ion beam extracted from a plasma, hot filaments, emitting electrons thermionically, are strategically placed on the downstream side of the extraction grid. Charge neutralization prevents spreading of the ion beam by Coulomb collisions among the ions. This work reports our observation that a self-neutralized ion beam can be obtained when the beam is extracted in the afterglow of a pulsed plasma. Specifically, a nearly monoenergetic ion beam was realized by applying a synchronous DC bias on an electrode in contact with the plasma (so-called boundary electrode) during a specified time window in the afterglow of a pulsed plasma. The ion beam flux in the pulsed plasma case was much higher than that in a continuous wave plasma under comparable conditions. Retarding Field Energy Analyzer measurements of the ion flux and IED with varying control parameters (including plasma pulsing frequency, and the time delay in the afterglow before a DC bias was applied on the boundary electrode) were performed to provide a plausible explanation of the system behavior.

Work supported by NSF.

### PS-TuP4 Gold Nanoparticle Catalyst for Plasma Nitridation of Thin Films, ***Takeshi Kitajima***, *Y. Kariya, T. Nakano*, National Defense Academy of Japan, Japan

Gold nanoparticles show a catalytic features which depends on its size.

We tried to apply the catalytic property of the gold nanoparticles to a thin film processing under a plasma exposure. The catalysis enhanced process has a possibility of a low damage plasma processing that eliminate ion bombardments and charge trapping.

The example of the process is Si nitridation using low pressure nitrogen plasma.

Gold nanoparticles are self-assembled on a $SiO_2$/Si(100) sample surface after the deposition of gold using an e-beam evaporator in an ultra high vacuum environment. After a 2 min. of gold deposition, hemispherical nanoparticles with the average width of 13.6 nm is formed. The number density of the nanoparticles is 6.0 e11 cm$^{-2}$ and most of the surface area is covered with gold.

Inductive coupled plasma of 50 MHz excitation and 30 mTorr of nitrogen pressure is exposed to the sample with gold nanoparticles on the surface. After the plasma exposure, the surface morphology of the sample shows increased uniformity of the gold nanoparticle size. The nitridation degree of Si is examined with XPS.

Due to the N1s XPS signal ratio to the other component like Si2p, O1s, Au4f and C1s, nitrogen composition on the surface is evaluated.

The nitrogen composition of the samples with and without gold nanoparticles is 6.2 and 5.0 % after the plasma exposure of 15 s.

Even though the direct ion exposure to the $SiO_2$ layer is inhibited by gold nanoparticles, Si sample is nitridated at similar rates with the aid of the catalytic effect of gold nanoparticles. The catalytic effect of the gold nanoparticles in this process is presumed to be the atomic transport of nitrogen atoms physisorbed on the nanoparticle surface to the underlined $SiO_2$ interface and subsequent chemical reaction to form SiON.

The process with nanoparticle catalyst is expected to perform on various atomic layer synthesis like graphene functionalization and so on.

### PS-TuP5 Development of Microwave Resonant Probes for Measurement of Plasma Density, ***Bo-Jr Chen***, *Y.C. Wu, J.S. Chiou, K.C. Leou*, National Tsing Hua University, Taiwan, Republic of China

Low temperature non-equilibrium plasma discharges are of great interests for applications ranging from micro/nano fabrication to bio/medical treatments. The density of the plasma discharge governs the basic characteristics of these plasma processes. In this study, microwave based diagnostics are developed for plasma density measurement or even process monitoring. The first device is a compact plasma absorption probe (C-PAP), a simple electric dipole like probe where the tip is formed by the center conductor of a coaxial semi-rigid cable, which is enclosed by a dielectric tube. The probe operated under the “resonant” mode, i.e., detecting the resonance frequency when the probing microwave and the nature frequency of the structure from by the probe and the surrounding plasma medium. The probe is designed by employing three dimensional electromagnetic numerical simulation analysis (HFSS, ANSYS Corp) where the plasma is treated as a dielectric with dielectric functions determined by plasma density, microwave frequency and collision frequency of electrons. The effects of plasma sheath and presheath are also investigated in the simulation analysis. The simulation results are used to calibrate the results from experimental measurements. The second resonant type probe under development is a spiral probe (SP) where the structure is a shorted microstrip transmission line. The first resonance of this structure occurs at the frequency where the transmission line becoming a half wavelength resonant structure. The spiral probe is designed for mounting on a chamber wall to minimize perturbation to the plasma discharges. Experimental and simulation results of the C-PAP, as well as the initial simulation analysis of the SP will be presented.

Acknowledgement

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### PS-TuP7 Molecular Dynamics Simulation of Ni Self-sputtering and Modeling of Interatomic Potential Functions, ***Nicolas Mauchamp***, *M. Isobe, S. Hamaguchi*, Osaka University, Japan

Plasma etching techniques have been widely used to manufacture semiconductor devices. Typical device scales of silicon (Si)-based field effect transistors (FET) are now approaching atomic scales. For the further development of plasma etching techniques to fabricate such small devices, a good understanding of plasma-surface interactions is indispensable. For example, during a plasma etching process with energetic ion bombardment, damages may be induced and lead to the formation of non-functional regions inside the created device structures. Therefore plasma-induced damages have to be avoided as much as possible.

In the production of magnetoresistive random-access memories (MRAM), stacks of thin layers of magnetic metals and insulators are deposited and etched to form magnetic tunnel junction (MTJ) cells. In typical manufacturing processes of MTJ cells, ion milling with energetic Ar+ ions are used. However, to further miniaturize MTJ cells and increase the MRAM integration, one would need less damaging and more selective etching processes for magnetic materials and insulators. The ultimate goal of this study is to establish reactive ion etching (RIE) processes for MTJ cells and we approach this goal by examining etching characteristics of magnetic materials with various reactive ions theoretically, using molecular dynamics (MD) simulations and first-principle quantum mechanical (QM) simulations. In this study, we take nickel (Ni) as a sample magnetic material.

In classical MD simulations, the interatomic potential models must be selected from the existing models or created based on QM simulation. It has been found that, with most existing interatomic potential models for Ni, the physical sputtering yields of Ni obtained from ion beam experiments for high ion incident energies cannot be reproduced by MD simulation. Therefore, in this study, we have focused on self-sputtering of Ni and examined the dependence of the self-sputtering yield on the interatomic potential functions. Since the Ni self-sputtering yield at a high ion incident energy sensitively depend on the short-range repulsive atomic interaction, we have determined the short-range interatomic functions based on experimentally observed Ni self-sputtering yields. It has been found that the newly adjusted interatomic potential model for Ni, which is based on the embedded atom model (EAM), can reproduce experimentally obtained Ni self-sputtering yields over a wide range of ion incident energy. Using the newly created interatomic potential model, we have also determined the dependence of the Ni self-sputtering yield on the ion incident angle.

### PS-TuP8 Atomic Layer Etching of Silicon Dioxide Using Alternating $C_4F_8$ and Energetic $Ar^+$ Plasma Beams, *S. Kaler, Q. Lou, V.M. Donnelly*, ***Demetre Economou***, University of Houston

Atomic layer etching (ALE) of $SiO_2$ was studied by alternating exposure of a 5 nm-thick $SiO_2$ film on Si substrate to (1) a plasma beam emanating from a c-$C_4F_8$ inductively coupled plasma (ICP), to grow a fluorocarbon (FC) film composed mainly of $CF_2$, and (2) an energetic (130 eV) $Ar^+$ ion beam extracted from a separate Ar ICP. *In-situ* X-ray photoelectron spectroscopy was used to analyze the chemical composition of the near-surface region, and to quantify the thickness of the FC and $SiO_2$ films. A very thin (3-6 Å), near self-limiting thickness $CF_2$-rich FC film was found to deposit on the $SiO_2$ surface with exposure to continuous or pulsed power $C_4F_8$ plasma beams, under conditions that generated a large relative flux of $CF_2$. Following this, a FC film of similar composition grew at ~10 times slower rate. Exposure of the thin film to the $Ar^+$ beam led to removal of 1.9 Å $SiO_2$. An estimated yield of 1.3 $SiO_2$ molecules-per-$Ar^+$ was found for a single ALE step. The rate of 1.9 Å/cycle persisted over multiple ALE cycles, but a carbon-rich residual film did build up. This film can be removed by a brief exposure to an $O_2$-containing plasma beam. Support from Lam Research and NSF is gratefully acknowledged.

### PS-TuP9 Si, $SiO_2$, and $Si_3N_4$ Etching Characteristics of Silicon Halide Ions ($SiF_x^+$, $SiCl_x^+$, and $SiBr_x^+$), ***Kazuhiro Karahashi***, *T. Ito, H. Li, Y. Muraki*, Osaka University, Japan, *M. Matsukuma*, Tokyo Electron Limited, Japan, *S. Hamaguchi*, Osaka University, Japan

Reactive ion etching (RIE) by halogen-based plasmas is widely used for etching of silicon-based materials such Si, $SiO_2$, and $Si_3N_4$ in semiconductor manufacturing processes. As semiconductor devices continue to be miniaturized, a better understanding of basic reactions of etching and/or deposition processes on substrate surfaces has become more important than before for finer controls of device structures in the manufacturing processes. In etching processes of silicon-based materials by halogen-based plasmas, Si atoms desorbed from the surface as etching products may enter the plasma (as ions such as $SiBr_x^+$ or charge neutral radicals such as $SiBr_x$) and return to the surface, forming an additional silicon-based material layer on the substrate as well as hard mask materials (such as $SiO_2$, and $Si_3N_4$). Therefore it is important to clarify etching characteristics of silicon-halides ions for Si, SiO2, and Si3N4 substrates for the development of highly controllable etching processes with halogen-based plasmas. Beam experiments of such etching processes offer useful information for a better understanding of interactions of individual species contained in a plasma with the surface. In this study, etching and/or deposition reactions of Si, $SiO_2$, and $Si_3N_4$ substrates are examined with the use of a mass-selected ion beam system, which can clarify the roles of silicon ($Si^+$), halogen ($F^+$, $Cl^+$, and $Br^+$), silicon mono-halide ($SiF^+$, $SiCl^+$, and $SiBr^+$), and silicon tri-halide ($SiF_3^+$,$SiCl_3^+$, and $SiBr_3^+$) ions for etching of Si-based materials. Si+ irradiation below 1000eV deposits silicon atoms on Si, $SiO_2$, and $Si_3N_4$ surfaces. Similarly, at sufficiently low incident energy, a silicon mono-halide ion beam also deposits silicon on the surface. The etching yield by silicon tri-halide ions is typically larger than three times the etching yield by single-halogen ions. Experimentally obtained etching yields or deposition rates for various combinations of Si-based substrates and incident silicon halides as functions of incident ion energy offer critical information for the further development of highly precise etching processes.

**PS-TuP10 The Interactions of Atmospheric Pressure Plasma Jets with Surfaces: *In Situ* Measurements of Local Excitations in Thin Films**, ***Eric Gillman***, Naval Research Laboratory, *B.M. Foley, J. Tomko,* University of Virginia, *D.R. Boris, S.C. Hernández,* Naval Research Laboratory, *A. Giri*, University of Virginia, *Tz.B. Petrova, G.M. Petrov,* Naval Research Laboratory, *P.E. Hopkins*, University of Virginia, *S.G. Walton*, Naval Research Laboratory

The energy flux to a surface during plasma exposure and the associated surface heating are of long standing interest as they contribute to the physicochemical changes associated plasma-based materials processing. The unique feature of plasmas compared to other methods of materials synthesis and processing is that the energy flux is delivered and absorbed at or very near the surface over short time scales, and thus requires fast, surface-sensitive techniques to fully appreciate the dynamics of the plasma-surface interface. To achieve this, we employ pump-probe Time-Domain Thermoreflectance (TDTR) to measure the electron and phonon excitation and energy transport dynamics in thin metal films during exposure to an atmospheric pressure plasma jet. The results show the energy delivered by the plasma jet causes a localized thermal spike that is dissipated radially from the point of contact. More specifically, energy delivered via the flux of particles and photons causes the kinetic energy of the electrons within the material to increase over an area commensurate with the plasma jet radius. That energy is then dissipated through electron-electron collisions and electron-phonon interactions as the excited electrons propagate radially from the point of contact. These results, in conjunction with plasma characterization, will be discussed in an effort to develop a first order understanding of energy transfer and relevant kinetics during plasma jet–surface interactions. This work is partially supported by the Naval Research Laboratory base program.

**PS-TuP11 Modeling of a Plasma Discharge in an ICP Plasma Source for a Strip Tool**, ***Vladimir Nagorny***, Mattson Technology, Inc., *V.V. Olshansky*, Kharkiv Institute of Physics and Technology, Ukraine, *S. Ma*, Mattson Technology, Inc.

Inductively coupled plasma (ICP) sources have been used in plasma processing for more than two decades, and will be used in a foreseen future. For a photoresist (PR) strip direct plasma interaction with a wafer is undesirable and plasma is used mainly for modification of a gas composition and creating chemically active radicals for processing the wafers. To achieve high ash rates strip tools usually operate at very high flows since a PR strip rate directly relates to the flux of radicals to the surface of the wafer.

Typical fluxes in strip sources are about or exceed 5slm per head and the gas pressure varies in the range of 0.5-5 Torr. At these high gas pressures, electron energy relaxation length for high energy electrons is very short and these electrons can only be in equilibrium with the local effective electric field $E_{eff}$ rather that with other electrons. That strongly affects both the distribution of energy deposition into plasma, rates of kinetic processes and the field penetration into the plasma volume. A high plasma density, high gas temperature (low gas density N) region is formed near the coil, where reduced electric field $E_{eff}/N$ is high enough to sustain the ICP discharge in a wide range of process gas pressures and flows, while outside of this region $E_{eff}/N$ is low and ionization is negligibly small.

In this presentation we compare results of plasma simulations in ICP strip source from the common model with drift-diffusion approximation for both electrons and ions and Maxwellian EEDF for electrons with similar simulations using a new model, where in the hot region the drift-diffusion approximation is used only for ions. As for electrons, they are considered in balance with the effective electric field, and the drift-diffusion approximation for them is used only outside the hot region.

**PS-TuP12 Characterization of Ion Lasers with Paschen Curves**, ***Steven Flores***, San Jose State University and Coherent Inc., *C. Fields*, Coherent Inc.

Paschen curves for argon and krypton are obtained by measuring the breakdown voltage of gases in an ion laser plasma tube. The data are taken at various pressures (voltages) with fixed electrode separations. Paschen curves can be used to determine the optimal setting of an ion plasma laser based on minimal breakdown voltage for a given plasma power. The Paschen curves vary with gas type and pressure. The trend lines can also be used to indicate the presence of impurities in the plasma.

**PS-TuP13 Plasma Simulation of Capacitively Coupled Plasma for High Aspect Ration Contact Process of Semiconductor**, ***Hyowon Bae***, Samsung Electronics Co. Ltd., *J. Kim,* Pusan National University, Republic of Korea, *M. Lin,* Hanyang University, Republic of Korea, *J. Um, S. Han, T. Kang,* Samsung Electronics Co. Ltd., *H.J. Lee,* Pusan National University, Republic of Korea

High aspect ration contact process has been important process to make dynamic random access memory(DRAM) and NAND flash memory with large sotrage and high speed. Plasma etching technology has been studied for few decades, and plasma uniformity or chemistry can be controlled on these days under some condition. However, plasma etching process is still very tough to obtain the result which we wish with high frequency up to 100 MHz and high power over 10kW. Therefore, control of plasma under these condition is required to be sucesseful plasma etching result, which leads to obtain almost same etching result at all area of wafer from center to the edge. It also promises high yield and high profit in the industry. Capacitively coupled plasma(CCP) is most popular method in etching and deposition process. Plasma simulation is performed in this study to obtain the plasma distribution for unifrom etch rate at all area. Under the specific condition, uniform plasma can be shown. Ion energy distribution, ion flux, and other physics will be explained in this presentation.

**PS-TuP14 $N_2$, $O_2$, and $NF_3$ Dissociation in a Low Frequency, High Density Plasma Source**, ***Hanyang Li***, *Y. Zhou, V.M. Donnelly,* University of Houston, *K. Wenzel, J. Chiu, J. Lamontagne, X. Chen,* MKS Instruments, Inc.

Most capacitive and inductive plasmas used in deposition and etching tools for semiconductor processing operate at pressures in the sub-Torr regime (typically <200 mTorr) at relative low power densities (~0.01 – 0.1 W/cm$^3$). Higher pressure, high power density plasma sources offer significant advantages in improved cost of ownership through increased tool throughputs, but have not received as much attention in the academic world. In this poster we present measurements of radical densities and gas dissociation fractions for various mixes of $N_2$, $O_2$, and $NF_3$ feed gases with Ar at 400 sccm total flow rate in a low frequency (400 kHz), high pressure (1-10 Torr), inductively-coupled toroidal remote plasma source from MKS Instruments operating at a power density of 5 – 50 W/cm$^3$. The radical densities and feed gas dissociation percentages in the plasma were measured by optical emission spectroscopy (OES), combined with Ar actinometry. The dissociation of $O_2$ drops from 55% to 10% with increasing $O_2$ percentage, while the dissociation of $N_2$ rises from 10% to ~100% with increasing $N_2$ percentage. For $NF_3$, the dissociation to form F rises with increasing $NF_3$ percentage from 60% at 1% NF3 and to 100% at 10% $NF_3$, while about 25% of the nitrogen is present as $N_2$, independent of $NF_3$ percentage, with presumably some or nearly all of the remaining nitrogen present as N atoms, which are detected in optical emission. Enhanced or suppressed dissociation as a function of added Ar will compared with changes in discharge current, relative electron density and other plasma parameters.

**PS-TuP16 Improvement of Adhesion Strength between Copper and Composite Materials using Plasma Press Method**, ***DooSan Kim***, *W.O. Lee, J.W. Park, M.K. Mun, K.S. Kim, K.H. Kim, Y.J. Ji, J.S. Oh, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Adhesion is one of the important issues for the wearable, attachable, and implantable devices. Especially, adhesion strength between hetero interfaces is very important. Various methods such as hot press, UV curing, thermal curing, and hot press after plasma treatment have been investigated to improve adhesion strength between different interfaces. But, for flexible devices, the adhesion strength obtained by these existing methods adhesion appear not enough and a higher adhesion force is required. In this study, in order to improve the adhesion strength between hetero interfaces, a novel plasma press method was introduced, and where, two interfaces are press bonded while plasma is on. The experiment was conducted in order to improve the adhesion strength between prepreg (Prepreg is a polymer substrate contained resin. Prepreg was also used as an insulating layer) and copper foil. These materials are used for the fabrication of multilayer flexible printed circuit board (PCB) substrate. The adhesion measurement was conducted by a peel off test. The plasma press method improved adhesion strength about 75 % compared to the conventional hot press method. The stronger bond for the plasma press is believed to be related to the formation of active carboxyl functional groups and unsaturated dangling bonds on the materials surfaces by the plasma operating during the hot press for bonding.

**PS-TuP17 Experimental and Simulation Study on Hydrogen Atom Kinetics in Low-pressure Capacitively Coupled Plasmas**, *S. Nunomura, K. Katayama,* ***Isao Yoshida***, National Institute of Advanced Industrial Science and Technology (AIST), Japan

In plasma processing, a hydrogen (H) atom is a key species (a radial) that strongly influences the gas-phase reactions and surface reasons. So, the investigation on H atom reaction kinetics is beneficial for controlling the gas-phase species and the material surface property. Here, we study the H atom generation and loss kinetics in low-pressure capacitively coupled plasmas (CCP).

We performed the H density measurement in CCP in two different configurations of electrodes: direct and remote configurations. In direct configuration, the processing material was exposed into the plasma, whereas in the remote configuration, the processing material was separated from the plasma by the metal mesh to reduce the ion bombardment and charging. The H atom density was quantitatively determined from vacuum ultra violet absorption spectroscopy (VUVAS) [1]. We found that the H atom density was strongly reduced across the mesh electrode in the remote configuration. For example, the H atom density was varied from $\sim 1\text{x}10^{10}$ $\text{cm}^{-3}$ in the discharge region to $\sim 1\text{x}10^{12}$ $\text{cm}^{-3}$ in the processing region for our mesh geometry of 0.2 mm thickness and 36% aperture ratio [2].

The fluid model simulations for CCP discharges have been performed to study the details of the H atom generation, diffusion and recombination kinetics [2]. The simulation yielded the H atom density of$\sim 1.0 \text{ x } 10^{12}$ $\text{cm}^{-3}$, which was in good agreement with that measured by VUVAS. The H atoms are generated mainly in the discharge region, via two processes: the electron impact dissociation ($e + H_2 \Rightarrow e + 2H$) and the ion-molecule reaction ($H_2^+ + H_2 \Rightarrow H_3^+ + H$). For the loss of H atoms, it is dominated by the surface recombination on the electrode. In the presentation, more details of experimental and simulation results are presented.

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**PS-TuP18 Effect of Superimposed Multi-frequency on Plasma Characteristics of an Inductively Coupled Plasma Source**, ***Kyung Chae Yang***, *H.S. Lee, S.G. Kim, D.I. Sung, M.K. Mun, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

To achieve reduced production cost and improved productivity for nanoscale semiconductor devices, the specifications of dry etchers have become more stringent. One of the important specifications for next generation plasma systems is the extremely high uniformity from center to edge of the substrate. Especially for inductively coupled plasma (ICP) sources, as the power to the ICP sources is increased for increased plasma density, non-uniform power deposition resulting in non-uniformity of the plasma has increased further. Recently, numerous theoretical and experimental studies have been performed to improve the plasma uniformity such as separate dual frequency excitation, very high frequency mixing, etc. However, controllability of a plasma uniformity over a large area substrate still remains as one of the major challenges.

In this study, as one of the methods in controlling the plasma uniformity, superimposed multi-frequency operation on an ICP source has been investigated. On the ICP source, dual frequency power selected from 2~ 40 MHz was applied and, on the substrate, a single frequency was applied, and the effect of power ratio of multi-frequency power on the plasma characteristics including the etch uniformity was investigated for a 300 mm diameter ICP etch system. The variation of multi-frequency power at a same total power changed the electron energy distribution profiles and plasma uniformity. When $SiO_2$ wafer was etched using $Ar/CF_4$, an improved etch uniformity by using a multi-frequency operation of the ICP source could be observed.

**PS-TuP19 Numerical Simulation of Capacitively Coupled Radio Frequency Plasma Discharges - Effect of Hollow Cathode Structure**, ***Hsin-Chang Chang***, *C.Y. Chen, P.S. Luo, K.C. Leou*, National Tsing Hua University, Taiwan, Republic of China

Radio frequency capacitively coupled plasmas (CCPs) are important plasma reactors for applications in a wide range of areas such as thin film deposition and dry etching, etc. The property of the discharge, e.g., plasma density and uniformity, can be tailored or enhanced by integrating the hollow cathode effect. In this study, fluid model numerical simulation is employed to investigate the effect of slots or holes on the grounded electrode, instead of the powered electrode as in conventional hollow cathode enhanced CCPs, on the discharge characteristics. Two different CCP reactors are investigated. The first one is an indirect $Ar/H_2$ CCP where a grounded mesh is placed between the two electrodes of a conventional CCP. The effect of the side of the holes on the plasma behavior, as well as the dependence of the ratio of ion to neutral radicals fluxes are analyzed. Simulation Results show that, as a result of the grounded mesh/grid that separating the two chambers, the flux of both ionic and reactive neutral species drop significantly, by a factor of ~1/1000 - 1/10000, from the top main chamber to the bottom drift chamber. This, in term, implies that the ion energy flux incident on the grounded bottom electrode should be minimal, and thus damage to the substrate surface due to ion bombardment can be significantly reduced. Moreover, simulation results show that hole size less than sheath thickness is needed for low ion flux toward substrate and low plasma potential in the bottom chamber. The second reactor we investigated is a CCP with a slot on the top grounded electrode while the bottom one is powered by rf voltage. Simulations are carried out for two different feed gases, Ar and $CF_4$. Results from parametric studies and comparisons of hollow cathode effect between electropositive and electronegative discharges will be presented.

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**PS-TuP20 Photocatalytic Effects of Ag-$TiO_2$ Nanotubes Fabricated by BCP Lithography**, *G.Y. Yeom*, ***Dain Sung***, *J.S. Oh, K.C. Yang, D.W. Kim*, Sungkyunkwan University, Republic of Korea

Titanium dioxide ($TiO_2$) is one of the multipurpose materials used for various functional applications such as solar photocatalysts for degradation of environmental contaminants due to its unique properties. Especially,environmental decontamination by photocatalysis using $TiO_2$ nanotubes can be more appealing than conventional chemical oxidation methods because of its low costs, nontoxicity, high surface-to-volume ratios, high surface activity, and simple recycling. In addition, noble metal nanoparticles, such as Ag nanoparticles, doped on the surface of $TiO_2$ nanotubes can increase their photocatalytic activities and can be easily fabricated by a photochemical deposition method under UV light irradiation. Among various methods to fabricate of $TiO_2$ nanotubes, $TiO_2$ nanotubes fabricated by using block copolymer (BCP) lithography and reactive ion etching (RIE) can form uniformly aligned nanoscale morphorlogies.

In this study, using the $TiO_2$ nanotubes fabricated with BCP lithography, $TiO_2$ atomic layer deposition (ALD), and RIE and Ag nanoparticles precipitated on $TiO_2$ nanotubes by a photochemical method, the photocatalytic effect of $TiO_2$ nanotubes with/without Ag nanoparticles was investigated by measuring the concentration change of a methylene blue solution. The photocatalytic effect of $TiO_2$ nanotubes was higher than flat $TiO_2$ film because of the increased $TiO_2$ surface area. Also, Ag nanoparticles attached on the $TiO_2$ nanotubes further improved the photocatalytic effect by facilitating electron–hole separation and promoting interfacial electron transfer process through the Ag nanoparticles. However, when the amount of Ag nanoparticles on $TiO_2$ nanotubes are too much, possibly due to the decreased UV penetration to $TiO_2$ by the increased surface area covered with Ag nanoparticles, the photocatalytic effect was decreased. By precipitating 7~9 nm size Ag nanoparticles for 20 min on 40~50 nm diameter/50~60 nm height $TiO_2$ nanotubes, the highest photocatalytic effect could be obtained.

**PS-TuP21 Prediction of Particle Generation by Machine Learning in Plasma Etching Tools**, ***Yoshito Kamaji***, Hitachi High-Technologies Corp., Japan, *M. Sumiya, A. Kagoshima*, Hitachi High-Technologies Corp., *M. Izawa*, Hitachi High-Technologies Corp., Japan

Prognostics techniques, which predict the remaining useful life of the components and monitor the health conditions of process equipment by utilizing data-sets that acquired from the sensors of equipment components, are gaining attention to solve the cost issues in semiconductor manufacturing. [1].

In this study, development of a prognostics system to predict the health conditions that deviated over time in microwave plasma etching tools was investigated. The selection of the right analytical engines for getting effective results has been a major issue that impedes deployment of prognostics techniques. Several machine learning algorithms including PCA-based T-squared /square prediction error (SPE) [2], self-organizing map (SOM) -minimum quantization error (MQE) [3], auto-associative kernel regression (AAKR) [4] were evaluated to predict particle generation for the etching of metal layers such as work function metals (WFMs). The benchmarking results indicated that AAKR and PCA-T squared most effectively captured particle generation and showed better monitoring performance compared with other algorithms. In addition, process parameters that affect the particle generation were clarified by calculating contribution values for each process parameter. Details will be discussed in this presentation.

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### PS-TuP22 Investigation of Wear-Resistance Enhancement of Plasma-functionalized Carbon-nanotube Composite Polyurethane Film

***Daisuke Ogawa**, H. Uchida, K. Nakamura,* Chubu University, Japan

We have investigated possible causes of mechanical enhancement for a composite polyurethane (PU) film with plasma-treated carbon nanotubes (CNTs). Wear-resistance is a main topic here in terms of mechanical property. Our preliminary result showed that wear-resistance was improved by means of making a CNT-composite PU film, in particular, in the case when the CNTs treated with the plasma, which is made with gas mixture of nitrogen and carbon dioxide, was utilized. In order to enhance such a mechanical property of PU, we considered the following two possibilities; the wear-resistance increased due to 1) a uniform spatial distribution of CNTs in a PU film and/or 2) the fact that plasma-treated CNTs gives additional wear-resistance from chemical aspects, possibly from functional groups on CNTs. In fact, it is known that isocyanate (NCO) group is sometimes utilized in order to enhance their mechanical property of PU. First, we observed our CNT composite PU films with optical microscopy. The observation showed that the spatial distribution of CNTs in a composite PU film was not really enhanced due to plasma treatment by comparing with other CNT composite PU film. The circumstance indicates that the plasma-treated CNTs enhances the wear-resistance of PU film possibly from chemical aspect. However, we know that this is still in the range of our speculation. Therefore, we have recently focused on making a direct identification of NCO groups on the plasma-treated CNTs. In this presentation, we will show our recent results whether or not our plasma-treated CNTs actually have NCO groups on CNTs, in particular more NCO groups on the CNTs treated with nitrogen and carbon dioxides than those with other plasma treatment. Here, we utilized acridine yellow (AY, $C_{15}H_{15}N_3$), which is a good indicator of NCO groups by using photoluminescence (PL). AY solution (2mg/L AY in tetrahydrofuran, THF, $C_4H_8O$) was added the solvent dispersing CNTs to attach AY and NCO groups. And then, the PL emission was observed. Our result showed that PL emission was observed from the samples relating with the CNTs exposed to the plasma made with nitrogen/carbon dioxide and only with carbon dioxide plasma. In fact, we did not expect to observe PL emission from the CNTs treated with carbon dioxide plasma because the lack of nitrogen species in this gas composition. However, the residue of air gas might have provided the species, and showing the emission. In this presentation, we will show more recent results and analysis of identification of NCO groups on CNTs.

### PS-TuP23 Dynamics of Power-Modulated Chlorine Plasmas

***Tianyu Ma**, T. List, P. Arora, Y. Zhou, V.M. Donnelly,* University of Houston*, S. Nam,* Samsung Electronics, Republic of Korea

Studies of power-modulated chlorine inductively-coupled plasmas will be presented. Power at 13.56 MHz applied to the plasma was modulated between a high power and low power state. This allows optical emission and actinometry with trace added Ar to be carried out during the entire period, unlike traditional pulsed plasmas where no power is input during the “low power” state. Optical emission spectra were recorded over the 200 to 900 nm region where emissions from Cl, $Cl_2$, SiCl, $SiCl_2$, $SiCl_3$ and Ar occur. The intensity of Cl-to-Ar emission, proportional to Cl number density, was strongly modulated, allowing Cl recombination coefficients to be obtained from a simple model. Langmuir probe measurements were also recorded. The plasma was found to operate in one of two modes. When power was dropped from high to low, ether 1) the plasma density and optical emission intensities quickly dropped to a lower level that then remained constant, or 2) the density dropped to a very low level, emission ceased for a rather long time until re-ignition occurred. Whether the plasma operates in mode 1 or 2 is sensitive to settings on the matching network and is also a function of pressure and modulation frequency.

Work supported by Samsung Electronics.

### PS-TuP25 Investigation of Electromagnetic Effects in Very High Frequency Linear Plasma Source

***Xiaopu Li**, K. Bera, J.A. Kenney, S. Rauf, K.S. Collins,* Applied Materials, Inc.

Very high frequency (VHF) capacitively coupled plasmas (CCP) are widely used for materials processing in the semiconductor industry. The spatial distribution of plasma in CCP discharges can be affected by electromagnetic effects. In this study, a VHF linear plasma source is considered, which consists of parallel metal bars enclosed within ceramic insulator tubes. The linear source is immersed inside the discharge volume, which is enclosed by a grounded metal box except for the input and output ports. A full three dimensional electromagnetic plasma model is used to understand the interactions between the external radio-frequency source and the plasma. The fluid plasma model computes species densities and fluxes, as well as the plasma current density. Drift-diffusion approximation is used for species fluxes in the continuity equations for all charged species. Neutral species concentrations are determined by solving the continuity equations with diffusion coefficients computed using the Lennard-Jones potentials. The electromagnetic phenomena are fully described by the Maxwell equations with the plasma current density updated from the fluid model. The RF source in the model excites a transverse electromagnetic (TEM) wave through the input ports. The CPML absorbing boundary condition is applied at the termination port to avoid electromagnetic wave reflections back into the plasma. The finite difference time domain (FDTD) technique is used to discretize the Maxwell equations, which are solved explicitly in time. Ar discharge is studied based on the reaction mechanism similar to the previous study [1]. The plasma density profile is found to be dependent on excitation frequency, pressure and power. The spatial distribution of plasma with in-phase and out-of-phase excitation from the ports is investigated as well.

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### PS-TuP26 Modeling of High-Density Magnetically Enhanced Inductive Plasmas Generated by Symmetrical Solenoid Coils

***Bocong Zheng**, M. Shrestha, Q.H. Fan,* Michigan State University

A magnetically enhanced inductive plasma source (MEIPS) was proposed to address the limitations of conventional inductively coupled plasma (ICP) sources. The MEIPS combined two solenoid induction coils wound in opposite directions and the grounded ends were positioned on the dielectric window. The capacitive coupling between the plasma and the coils was subsequently minimized. The induction coils created a confined magnetic field within the plasma region, leading to a significant increase in the energy-coupling efficiency. To understand the plasma characteristics under different conditions, the MEIPS discharges were modeled and compared with a conventional planar coil ICP discharge. It was found that the MEIPS could generate a much higher plasma density than the conventional ICP discharge under the same input power. By inserting a ferrite core into the coils, the MEIPS discharge could ignite at ~2 MHz and the plasma density dramatically increased with the increase in the frequency until ~6 MHz. Then the plasma density decreased gradually as the frequency further increased due to the dramatically reduced permeability at high frequencies. Comparing with an air core, the ferrite core led to more stable magnetic field distribution with a higher maximal flux denisty ***B***.

### PS-TuP27 Plasma Modeling in the OpenFOAM Framework

*A.K. Verma,* ***Venkattraman Ayyaswamy**,* University of California Merced

As emphasized in the 2012 Roadmap for low temperature plasmas (LTP), scientific computing has emerged as an essential tool for the investigation and prediction of the fundamental physical and chemical processes associated with these systems. While several in-house and commercial codes exist, with each having its own advantages and disadvantages, a common framework that can be commonly developed by researchers from all over the world will likely accelerate the impact of computational studies on advances in low-temperature plasma physics and chemistry. In this regard, we present a finite volume computational toolbox to perform high-fidelity simulations of LTP systems. This framework, primarily based on the OpenFOAM solver suite, allows us to enhance our understanding of multiscale plasma phenomenon by performing massively parallel, three-dimensional simulations on unstructured meshes using well-established high performance computing tools that are widely used in the computational fluid dynamics community. In this talk, we will present preliminary results obtained using the OpenFOAM-based solver suite with benchmark three-dimensional simulations of microplasma devices including both dielectric and plasma regions. We will also discuss the future outlook for the solver suite.

### PS-TuP29 The Role of Charge Exchange Collisions in Selective Etching of Si

***Sergey Voronin**, P. Biolsi,* TEL Technology Center, America, LLC*, A. Ranjan,* Tokyo Electron Miyagi Limited, Japan

Continuous shrinkage of transistors in sub-7nm technological nodes requires new integration and etching challenges. As the direct scaling of the FinFET to 5nm is extremely difficult, the use of a 3D integration scheme is considered to be a prospective way toward the next technological node. In addition to generic process requirements (high anisotropy, minimum CD loading and high selectivity to the mask films), conductor etching in such structures is more complicated due to different positions of the stopping layers. Features with deep etch targets may face underetching, while features with short targeted depths may have severe notching due to excessive positive charge of the stopping layer. Fast neutral beam processing in ion-assisted reactive etching is one of the ways for the induced charge mitigation and to eliminate this unwanted effect.

We report a study of Si etching in an HBr/Ar surface-wave Radial Line Slot Antenna plasma. The ability of RLSA$^{TM}$ plasma etchers to operate in a very wide range of the pressures allows the etch process well above 100mT. Process operation in this high pressure range and large Ar$^+$-Ar charge-exchange cross sections (~3x10$^{15}$ cm$^{-2}$ at 100’s eV) result in numerous charge exchange collisions in the plasma sheath, leading to a significant presence of the fast neutrals.

A simple model for the ion and neutral energy distributions in an HBr/Ar plasma discharge has shown a significant input of the neutral ion beam. With the exception of the results for the hydrogen and bromine ions, the calculated fast neutral fluxes for Ar can be up to 70% of the total ion flux with the energies comparable to the ions. Reducing operating pressures below 50mT with increase in the plasma density provides etching mostly caused by ions. This correlates well with the experimental etch profiles suffered from notching and bowing.

**PS-TuP30 Development of an Aluminum Nitriding Process using Electrostatic Plasma Mass Spectroscopy and Energy Analysis and In Vacuuo Auger Electron Spectroscopy**, ***Christopher Muratore***, m-Nanotech Ltd., University of Dayton, *A. Korenyi-Both*, Tribologix Inc.

Aluminum nitride is a hard, wear resistant surface. Modifying an aluminum alloy surface by diffusion based plasma treatment is one potential approach for increasing the wear resistance of aluminum components, however, a review of the literature and discussion with industrial nitriding operations reveal that there are a number of challenges associated with this task. The primary challenge is initial removal of the native oxide formed spontaneously on aluminum surfaces, and inhibiting its formation during the process, even at high vacuum. Using a novel plasma nitriding process,thick aluminum nitride layer (>1 micron) was produced on 6061-T6 alloy samples. Key steps included removal of the oxide layer and identification of pulse characteristics fpr the applied power to the cathode. These steps were accomplished using unique in situ process diagnostics including Auger electron spectroscopy to identify the time and conditions required to clean the aluiminum surface and plasma mass spectrometry and energy analysis to identify the optimum ratio of atomic nitrogen atoms compared to molecular nitrogen ions, as identified in prior works for nitriding of stainless steel. It is observed that maximizing the number of atomic nitrogen ions yields higher nitriding rates for aluminum.

**PS-TuP31 A New Transformer Model for Solenoidal ICP Discharge Expandable to Low Density Plasma**, ***Jang-Jae Lee***, *S.J. Kim, K.-K. Kim, Y.S. Lee, S.J. You*, Chungnam National University, Republic of Korea

A transformer model is well known as model for the analysis of the physics of inductively coupled plasma source. However, this model can be applied only at high density region where the skin depth is much smaller than the chamber radius. In this study, a transformer model which can be applied even under long skin depth conditions was presented. The expression of fields in the plasma source is derived in a one-dimensional geometry and the circuit components of transformer model as a function of electron density can be obtained by the spatial integrating the fields. Comparing these results with those obtained from Maxwell’s equation, we confirmed that the results agree with each other in various conditions.

**PS-TuP32 Development of a Novel VI Sensor for RF Power Measurement**, ***Kwang-Ki Kim***, *S.J. You*, Chungnam National University, Republic of Korea

VI sensor plays an important role in dynamic impedance matching in RF power systems for various plasma fabrication processes. Therefore, many kinds of VI sensors have been developed for several years. However, these sensors have an issue of VI coupling that a transformer coil only for detecting current also detects voltage which is for detecting of a voltage sensor. In order to reduce the voltage in the coil, we used a novel double shielding walls that can shield the voltage from the coil effectively. We confirmed a voltage and current ratio in the coil using an electro-magnetic simulation by changing the walls' height, position and gap between the walls then analyzed to find VI coupling minimization condition. We developed highly well VI decoupled sensor that has a phase difference about 1.32 degrees between the voltage and current compare to the other sensor that has the phase difference above 20 degrees in a condition of ideally phase difference zero.

**PS-TuP33 Transmission Line Model of Cutoff Probe**, ***Si-Jun Kim***, *J.-J. Lee, K.-K. Kim, Y.S. Lee,* Chungnam National University, Republic of Korea, *D.W. Kim,* Korea Institute of Machinery and Materials, Republic of Korea, *J.H. Kim,* Korea Institute of Standards and Science, Republic of Korea, *S.J. You,* Chungnam National University, Republic of Korea

Transmission line(TL) model was applied to cutoff probe(CP), which is a microwave resonance probe for measuring electron density. Application of preceding model(circuit model) for analysis of characteristics of CP was limited to low electron density regime(< 1010 cm-3). In order to supplement the circuit model we introduced TL model and compared results between TL model and three-dimensional full-wave electromagnetic(3-D FWEM) simulation. Simulation results of TL model are in good agreement with that of the a 3-D FWEM simulation in both low and high electron density regime. Furthermore the results of TL model are the same with that of circuit model in the low electron density regime. Therefore by using TL model we can expand the applicable range of cutoff probe up to high electron density regime.

**PS-TuP34 Fault Detection in Radio-frequency Plasma Processing using Voltage-current (VI) Probes and Statistical Models**, ***Thomas Gilmore***, Impedans Ltd, Ireland

Radio-frequency (RF) voltage-current (VI) probes, mounted between the matching network and plasma reactor, can accurately detect plasma impedance changes at the fundamental and harmonic frequencies. The plasma impedance is very sensitive to any electrical, mechanical and/or geometrical changes that may occur in the reactor. The nonlinear nature of the plasma impedance generates a rich harmonic spectrum, accurate measurement of which can be used to precisely detect faults that affect the electrical, geometrical or mechanical integrity of the plasma process. Examples of such faults include; electrical integrity of the RF connections, misplaced substrates, broken focus rings, leaking valves, plasma confinement issues and parasitic plasma formation.

In this poster, we summarize the results of fault detection studies across several RF processes and across a number of industry sectors. It was found that for certain gross faults, such as plasma not igniting, the fundamental voltage, current, and phase angle are sufficient for detection. However, many fault types are more subtle. For example, a wafer misplaced by less than a millimeter off-centre does not show any significant deviation in the fundamental parameters. Higher order harmonics, on the other hand, can show significant variation. It was found that the exact harmonic properties (voltage, current or phase) that are sensitive to the fault are also process and reactor dependent.

The statistical approach used relies on a preliminary baseline measurement of a faultless process across the full spectrum of parameters detected by the RF VI probe. The analysis runs continuously and a Z-score technique is applied to all parameters. A deviation from the “normal” is considered significant if it exceeds six standard deviations (Six Sigma). Data from live semiconductor wafer production will be presented showing fault detection due to wafer misplacement. Charts of various other faults and their significance in terms of sigma-number will also be presented for other processes. This approach can be used to implement alarms on plasma processing tools when faults are detected, preventing costly product scrappage events.

**PS-TuP35 Finding Adequate Global Model of Non-Maxwellian Distribution based on PIC Simulation**, ***Young-Seok Lee***, *S.J. Kim, J.-J. Lee, S.J. You*, Chungnam National University, Republic of Korea

The electron energy probability function (EEPF) is usually assumed to be Maxwell distribution for 0-D global model. Meanwhile, it is well-known that the form of EEPF of Ar plasma changes from bi-Maxwellian to Druyvesteyn as the gas pressure increases. Thus, to apply the 0-D global model of Maxwellian distribution to the non-Maxwellian plasma, we weighted up the relative contribution of two distinct electrons with different temperatures. The contributions of cold/hot electrons to the power and particle balance were investigated by comparing the result of the global model considering all combinations of electron temperatures with that of 1-D particle-in-cell Monte Carlo collision (PIC-MCC) simulation and the result of investigations was analyzed physically. Furthermore, predictions consistent with PIC-MCC simulation for variations of the contribution of cold/hot electrons at different pressures and driving currents are presented.

## Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
## Room: Central Hall - Session SA-TuP

## Synchrotron and FEL-Based Analysis Poster Session

**SA-TuP2 Inelastic Background Analysis using a Reference on Technologically Relevant Samples: Determination of Input Parameters**, ***Charlotte Zborowski***, *O.J. Renault,* CEA/LETI-University Grenoble Alpes, France, *A. Torres,* CEA/LETI-University Grenoble Alpes, Francee, *Y. Yamashita,* NIMS, Japan, *G. Grenet,* Inl, Ecl, France, *S. Tougaard*, SDU, Denmark

**Abstract:** Recently, the advent of Hard X-ray Photoelectron Spectroscopy (HAXPES) has enabled to study deeply buried interfaces [1,2]. It was shown that by combining HAXPES with inelastic background analysis [3], structures at a depth >50 nm can be studied. This study was performed on technologically relevant High Electron Mobility Transistors presenting different thicknesses of the Ta/Al electrode on an $Al_{0.25}Ga_{0.75}N$/AlN/GaN heterostructure. HAXPES was performed at the Spring-8 synchrotron using 8 keV photons. Here, we present a non-destructive solution to get information on deeply buried layers and interfaces. This is a refined analytical method, based on the use of a reference spectrum, for determining the required input parameters, i.e. the inelastic mean free path calculated using the TPP-2M formula and the inelastic scattering cross-section. As the spectra present marked plasmons, after the elastic peaks, we used an average of individual inelastic scattering cross-sections [4], K, which can be determined from Reflection Electron Energy-Loss Spectra. The use of a reference sample gives extra constraints which make the analysis faster to converge towards a more accurate result. The results were determined with the best Ta $3p_{3/2}$ corrected spectra calculated with different cross-sections and the resulting in-depth distribution was found with an accuracy better than 5% and in good agreement with the TEM results. We have also successfully used this technique to study structures at a depth >70 nm.

**References**

[1] P. Risteruci et al., Applied Physics Letters, 104, (2014).

[2] C. Zborowski et al., Applied Surface Science, (Submitted).

[3] S. Tougaard, Journal of Electron Spectroscopy and Related Phenomena, 178–179 (2010).

[4] P. Risterucci et al., Applied Surface Science, 402, (2017).

*Part of this work was performed at the Nanocharacterization Platform of CEA-MINATEC. NIMS and Spring-8 are acknowledged for providing beamtime and the staff of the BL15-XU beamline for their assistance during the experiment.*

**SA-TuP3 Hard X-ray Photoelectron Spectroscopy in the Home Laboratory: A Commercially Available System**, ***Susanna Eriksson**, P.P. Palmgren, M.P. Patt, M.H. Heiss, P.B. Baumann, P.Z. Zeigermann, P.W. Wiell, K.B. Backlund, C.L. Liljenberg, M.L. Lundqvist*, Scienta Omicron

During the past decade, increased attention has been shown to hard X-rays in the photoelectron spectroscopy field. This is mainly due to the increased information depth enabled by the higher photon energies. Such bulk sensitive measurements could previously only be performed at dedicated synchrotron radiation facilities. The beam lines providing this type of radiation are heavily booked, so access to the experimental setups is thus limited.

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

At the heart of the system is a liquid jet of a molten Ga-rich alloy. Electrons which are accelerated into this jet generate an intense Ga Ka radiation. These X-rays are monochromized and refocused using an ellipsoidal mirror in a Rowland geometry. The small spot size of 20 µm provided by the liquid jet source is maintained throughout the passing of the monochromator and only slightly broadened to about 50 µm. The photon energy width is targeted at 0.5 eV, suitable for the typical intrinsic core level width at the relatively high photon energy. In order to allow for easy adjustment of the X-ray focal point relative to the electron analyzer, the entire assembly of monochromator and source can be moved down to a precision of a few micrometers. The hemispherical electron analyzer is configured for high kinetic energies allowing for detection of the full energy range the source provides, a large acceptance angle of +/- 30 degrees

We present prototype data taken from polycrystalline gold and silicon wafers with a surface layer of silicon dioxide with a controlled thickness.

**SA-TuP4 Vacuum System of the ESS Cold Linac, Update on Design and Status**, ***Fabio Ravelli**, S.M. Scolari, M.J. Ferreira,* European Spallation Source ERIC, Sweden

The European Spallation Source, under construction in Lund (Sweden), is a neutron source based on a 5 MWatt super-conducting linear accelerator. The ultimate goal of ESS is to be the brightest neutron scattering facility and to enable novel science in many fields, such as biology research, environmental technologies and fundamental physics.

After a brief description of the superconducting Linac, the talk focuses on the vacuum design of the Warm Units that give continuity to the beam line environment between adjoining cryomodules [1]. As the use of N on-Evapoarble Getter and Sputter Ion P ump comb ination pumps is under evaluation, a campaign of measurements on particles generated during operation (activation - regeneration - pumping) by two different models of combination pump has been performed; the results of these tests are discussed. Finally, some insights about particle free installation tooling [2] are presented.

[1] ESS Vacuum System Status, Dr. Marcelo J. Ferreira, ESS Vacuum System Section Leader, IVC-20, August 21-26, 2016, Busan, Korea

[2] Particle Free Installation of Warm Linac Units at ESS F. Ravelli and M. J. Ferreira, 2016 CAS Accelerator School, October 2-14, 2016, Budapest, Hungary

## Scanning Probe Microscopy Focus Topic
## Room: Central Hall - Session SP-TuP

### Scanning Probe Microscopy Poster Session

**SP-TuP1 Pycroscopy – A Community-Driven Software Package for Analyzing Microscopy Data**, *S. Somnath,* ***Chris Smith****, S. Jesse, R. Vasudevan, N. Laanait*, Oak Ridge National Laboratory

Microscopy and material science are undergoing profound changes, driven by experimental datasets that are rapidly growing in dimensionality and size, increased accessibility to high-performance computing (HPC) resources, and more sophisticated computer algorithms than ever before. These changes are most pronounced in the functional imaging of materials. However, the softwares supplied with instruments such as microscopes are typically very expensive, do not provide access to advanced or user-defined data analysis routines, and store data in proprietary formats. Furthermore, these proprietary software and data formats not only impede data analysis but also hinder continued research and instrument development, especially in the age of “big data”. Therefore, moving to the forefront of data-intensive materials research requires general and unified data curation and analysis platforms that are community driven and HPC-ready.

We have developed a platform called Pycroscopy that uses community-driven approaches for analyzing and storing data. Pycroscopy is freely available via popular software repositories, and therefore lifts any financial burden for handling data. Pycroscopy uses an intuitive data structure stores data in and hierarchical data format (HDF) files that can be interrogated using any programming language, scales well from kilobyte to terabyte sized datasets, and can readily be used in HPC environments unlike proprietary data formats. More crucially, Pycroscopy uses a universal data format that is curation-ready and therefore both meets the guidelines for data sharing issued to federally funded agencies and satisfies the implementation of digital data management as outlined by the United States Department of Energy. This instrument-independent data format has also greatly simplified the correlation of data acquired from multiple instruments, necessary for comprehensive studies of materials. Unlike many other open-source packages that focus on analytical or processing routines specific to an instrument, the general definition of the Pycroscopy data format can be readily adopted for different microscopy techniques. Furthermore, the generality of Pycroscopy provides material scientists access to a vast and growing library of community-driven data processing and analysis routines that far exceed those provided by instrument manufacturers and are desperately needed in the age of big data. In summary, Pycroscopy can greatly accelerate materials research and discovery through the realms of big, deep, and smart data.

## Surface Science Division
## Room: Central Hall - Session SS-TuP

### Surface Science Poster Session

**SS-TuP1 Self-assembly of Organic Thin Films on Metal Surfaces**, ***David Wisman***, Indiana University, Department of Chemistry and NSWC Crane*, C. Tempas, T. Morris,* Indiana University*, S. Kim, D. Lee,* Seoul National University*, S.L. Tait,* Indiana University Department of Chemistry

Organic semiconductors have the potential to replace silicon in some electronic devices because they require less stringent production environments and can offer new functionalities, such as flexible devices. One major drawback of organic semiconductor films is their inefficient charge transport. In traditional organic film materials, the molecules only lay flat in the first few molecular layers before transitioning to less favorable geometries for charge transport. Previous work published in our group has shown that the tris(N-phenyltriazole) (TPT) molecule on a Ag(111) surface shows planar stacking through more than 20 molecular layers due to the π-π donor-acceptor intermolecular contacts between the electron-deficient tris(triazole) core and electron-rich peripheral phenyl units. Scanning tunneling microscopy (STM) studies of this molecule show that it does not change its packing structure through the >20 molecular layers studied. Here, we present investigations of derivative molecules of TPT which have different electron distributions and structures to investigate their effect on stacking. We compare the monolayer packing of these derivative molecules to that of TPT by molecular-resolution STM analysis and then investigate multilayer stacking properties of these molecules. Comparison conductivity measurements for TPT, and the two derivative molecules are compared with pentacene using four-point conductivity measurements. These studies may lead to new organic semiconductor material designs that have well-controlled structure and increased charge transport, making them more competitive with traditional silicon devices.

**SS-TuP2 Periodic Modulation of Graphene by a 2D-FeO/Ir(111) Moiré Interlayer**, ***Yujing Ma***, *M. Batzill*, University of South Florida

Ultrathin films of iron oxide form a two-dimensional (2D) FeO layer on Ir(111). Due to difference in lattice constant between 2D-FeO and Ir(111) a moiré superstructure is formed. We studied the 2D-FeO/Ir(111) structure by soft X-ray photoelectron spectroscopy(XPS), X-ray photoemission diffraction(XPD), and low energy electron diffraction(LEED), and scanning tunneling microscopy(STM). Moreover we show that this 2D-FeO layer may also be grown by iron intercalation and subsequent oxidation underneath a graphene layer on Ir(111). Thus the graphene can be decoupled from the metal by the 2D-FeO layer. Changes in the graphene C 1s binding energy can be attributed to shifts in the Fermi level of graphene as a consequence of interface band alignment for weak interactions between graphene and the substrate. A shift of C 1s to lower binding energy, for graphene supported on FeO/Ir(111), is a consequence of the dipole moment in the 2D-FeO layer normal to the Ir(111) surface. Broadening of the C 1s peak is consistent with a locally varying 2D-FeO dipole within the moiré structure and thus implies a modulated charge doping of the graphene.

**SS-TuP3 CO Oxidation on Single and Multiple Layer PdO(101) Structures Grown on Pd(100)**, ***Vikram Mehar***, *C. Wu*, University of Florida, Gainesville, *M. Shipilin*, *E. Lundgren*, Lund University, Sweden, *H. Gronbeck*, Chalmers University of Technology, Sweden, *A. Ashtagiri*, The Ohio State University, *J.F. Weaver*, University of Florida, Gainesville

Palladium has been extensively used to promote the catalytic combustion of methane and CO oxidation in automotive exhausts. It has been observed that formation of metal oxide layers can significantly alter the surface reactivity due to differences in chemical properties of oxide and metal surface. Understanding the reactivity of oxides formed under different growth conditions could facilitate the design of catalysts attuned for specific applications. In this presentation, I will discuss results of our studies of Pd(100) oxidation by atomic oxygen as well as the adsorption and oxidation of CO on single-layer and multilayer PdO structures. We find that a well-ordered PdO(101) film of about 7 ML thickness develops on Pd(100) during oxidation with O-atoms at 500 K, whereas a thicker PdO structure (~14 ML) with an apparently more rough morphology grows at temperatures above 600 K. LEED shows that the multilayer PdO(101) structure adopts the same epitaxial relationship with the Pd(100) substrate as the so-called √5 surface oxide, which has been previously shown to correspond to a single layer of PdO(101).

Although the surface structures are nominally identical, temperature-programmed reaction spectroscopy (TPRS) and reflection-absorption infrared spectroscopy (RAIRS) measurements show that the single layer and multilayer PdO(101) structures exhibit distinct reactivity toward CO. TPRS shows that the multilayer PdO(101) structure is more reactive toward CO compared with the single layer PdO(101). Also, RAIRS shows that CO binds only in an atop configuration on the coordinatively-unsaturated (cus) Pd atoms of the multilayer PdO(101) structure, whereas CO initially populates bridging Pd sites on the single PdO (101) layer before also occupying atop Pd sites at higher CO coverages. I will also present results of density functional theory calculations that clarify the origins the different chemical reactivity of the single and multiple layer PdO(101) structures toward CO.

**SS-TuP4 Evaluation of Dynamic Wettability on 2D Inverse Opal Structure**, ***Naoya Yoshida***, *T. Genma*, *K. Fukasawa*, *T. Okura*, Kogakuin University, Japan

Static wettability of smooth solid surface is determined by balance of surface energy of each solid-liquid, liquid-gas, and solid-gas interface, and surface roughness. However, dynamic wettability is thought to be involved by various factors, *e. g.*, the non-uniformity of composition and surface structure. We fabricated inorganic oxide surface with 2D inverse opal structure and homogeneity of the composition and surface structure, and evaluated their static and dynamic wettabilities.

At first, uniformed 2D colloidal particle film was fabricated on a glass substrate in the similar manner to LB method. $SiO_2$ thin films with 2D inverse opal structure were fabricated by using a precursor solution (tetraethoxysilane in ethanol and 2-ethoxyethanol) by spin coating and heating at 500°C. The prepared samples were stored in a constant temperature and humidity chamber. These samples were characterized by scanning electron microscope (SEM), optical microscope, and contact angle meter.

SEM images of fabricated samples are shown in figure 1. Film thickness and structure were different depending on the concentration of the precursor solution. Wettability seemed to depend on the film structure, especially in terms of dynamic wetting process; on several samples, thin water film was obviously observed at the outside of a droplet edge. Furthermore, pinning of a water droplet by large defects was also observed.

We fabricated $SiO_2$ thin films with various 2D inverse opal structures, and their static and dynamic wettabilities were evaluated. In this presentation, details of them and wetting processes will be discussed.

**SS-TuP5 Direct Attachment and *In Situ* Metalation of 29,31-H Phthalocyanine on Chlorine-terminated Si(111) Surface**, ***Chuan He***, *A.V. Teplyakov*, University of Delaware

The attachment of phthalocyanine molecules to solid surfaces has attracted substantial attention due to the unique physical and chemical properties of the resulting interfaces, which can be further tuned by designing chemical schemes to tether the phthalocyanine moieties by strong covalent bonds. Furthermore, the properties of these interfaces can be tuned and controlled even further by varying the coordinated metalation, thus providing a wide variety of platforms for many applications, including catalysis and sensing. In this work, an efficient wet chemistry method is developed to achieve the covalent attachment of phthalocyanine molecules directly to a chlorine terminated Si(111) surface without any additional linkers or functional groups. The possibility of cobalt metalation of this modified surface is also tested. X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and atomic-force microscopy (AFM) are utilized to study the phthalocyanine attachment and metalation processes. The theoretical predictions of core-level N 1s binding energies are investigated by density functional theory (DFT) calculations to compare with experimental results obtained by XPS and to infer the possible mechanisms of surface reactions.

**SS-TuP6 Structural Growth and Oxidation of $TbO_x$ Thin Films on Pt(111)**, ***Christopher Lee***, *V. Mehar*, University of Florida, *S. Keil*, *V. Zielasek*, *M. Bäumer*, University of Bremen, Germany, *J.F. Weaver*, University of Florida

Within the family of rare earth oxides (REOs), the terbium oxides exhibit favorable properties in selective oxidation catalysis due to the flexibility in the storage and release of oxygen within the lattice, specifically through structural rearrangement into well-ordered intermediates between the $Tb_2O_3$ and $TbO_2$ stoichiometries. We investigated the growth and structures of $TbO_x$ films grown on Pt(111) in ultra-high vacuum (UHV) as well as the oxidation of the films by plasma-generated gaseous atomic oxygen. LEED and STM show that the deposition produces crystalline $Tb_2O_3$ films that adopt an oxygen deficient cubic fluorite structure where the film conforms to the hexagonal registry of the Pt(111) substrate. This is characterized by initial surface wetting up to 2 ML of $Tb_2O_3$ followed by 3D Stranski-Krastanov island growth at higher coverages.

We also find that the terbia film undergoes isomeric reorganization into the longer-order bixbyite $Tb_2O_3$ conformation when subject to a combination of atomic oxygen exposure along with subsequent annealing at 1000 K. LEED and TPD show that coexisting, ordered intermediates between $Tb_2O_3$ and $TbO_2$ may then be created by further oxidizing the bixbyite $Tb_2O_3$ film via atomic oxygen beam exposure. In particular, two distinct $O_2$ desorption peaks in TPD spectra provide evidence of the sequential phase stabilization of $Tb_7O_{12}$ (ι-phase) and $Tb_{11}O_{20}$ (δ-phase) along with lower temperature peaks corresponding with more weakly bound surface oxygen. The rapid reorganization of oxygen and oxygen vacancies within this intermediate regime is promising in that it suggests that specific structural arrangements of the terbia lattice may readily adjust to accommodate dissimilar metal cations into the metallic lattice to stabilize ordered, substitutionally doped films. The future outlook is to characterize structure and promoted surface chemistry of doped terbium oxide films, particularly the changes in oxidation induced by the incorporation of high valence dopants and low valence dopants into the metallic framework of the oxide. The larger implication is that the substitutional doping of terbium oxides can provide fundamental insight into doped oxide catalysis, which can provide the additional degree of tuneability towards increased reactivity or selectivity towards partial oxidation pathways required for an effective oxidative coupling of methane (OCM) catalyst.

**SS-TuP7 Surface Spectroscopy and Thermal Desorption Studies of Sulfur-Doped Tungsten Oxide**, ***Anthony Babore***, *J.M. Langford, J.C. Hemminger*, University of California Irvine

Mixed sulfide/oxide films were prepared on W (100) as a model system for sulfur-doped tungsten trioxide which has shown potential for enhanced visible light absorption for photocatalysis. In this study we sought to gain a fundamental understanding of the effects of incorporating sulfur atoms into a tungsten oxide system. This was accomplished using a combination of temperature programmed desorption (TPD), Auger electron spectroscopy (AES) and high-resolution electron energy loss spectroscopy (HREELS). $D_2O$ was used as a probe molecule in the TPD experiments and yielded pronounced effects on the desorption spectra for pure oxide, sulfide and mixed sulfide/oxide films on W (100). In addition coverage dependent desorption energies were calculated and compared. AES spectra displayed the relative amounts of sulfur and oxygen on the surface and HREELS experiments confirmed the presence and thermal stability of tungsten sulfide on the surface.

**SS-TuP8 Preparation and Characterization of Metal-doped Calcium Phosphate**, ***Yuki Iwai***, *N. Yoshida, T. Okura*, Kogakuin University, Japan

Ti-doped Hydroxyapatite (TiHAp) partially substituted $Ca^{2+}$ with $Ti^{4+}$ exhibits excellent photocatalytic decomposition of organic compounds, as $TiO_2$ shows. Although the mechanisms of phtocatalytic activities of TiHAp are still unclear, Ti-doping and/or defects derived from Ti-doping are thought to be important in photocatalytic reactions. Here, we tried to fabricate beta-tricalcium phosphate (β-TCP), with substitution of Ca sites or $PO_4$ sites with M or $MO_4$ (M = Ge, Zr, Nb, Mo, Sn, W), respectively, and to study the effect on crystal structure and photocatalytic activity.

M-doped β-TCPs were prepared by solid-state or coprecipitation methods. By solid-state method, $CaCO_3$ and $CaHPO_4 \cdot 2H_2O$ with $GeO_2$, $Nb_2O_5$, or $SnO_2$ (Ca / (P + M) = 1.50, M / (P + M) = 0.01~0.03) were mixed with an alumina mortar. Samples were obtained after calcination at 1000°C for 10 h. By coprecipitation method, $Ca(NO_3)_2 \cdot 4H_2O$ and $H_3PO_4$ with $ZrCl_2O \cdot 8H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, or $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$ (Ca + M) / P or Ca / (P + M) = 1.50, M / (Ca or P + M) = 0.01~0.10) were dissolved in ion-exchanged water, and stirred for a while. After that, dil. $NH_3$ aq. was slowly added to the solution until pH became 9.5. The precipitation was filtered, dried at 100°C, and calcinated at 1000°C for 24 h. The obtained powders were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscope (SEM) measurements.

XRD measurements indicated that the samples were mainly β-TCP. In the case of Zr, Mo, and W doping, the obtained samples exhibited β-TCP single phase at low doping concentrations. Against doping of Ge, Nb, and Sn, β-TCP was obtained with other phases such as hydroxyapatite (HAp). In this presentation, structure, adsorption of organic/inorganic compounds, photocatalytic activity will be also discussed.

**SS-TuP9 Multiscale Investigation of Catalytic Activity of Ultra-Thin Molybdenum Nitride for Hydrogendenitrogenation Process**, *W.E. Kaden*, ***Asim Khaniya***, University of Central Florida

Hydrogendenitrogenation (HDN), a process of removing organonitrogen compounds from petroleum or coal-derived feedstocks, is one of the hydro treating processes in the oil refinery industry. Carefully executed studies on transition metal nitrides, mainly in molybdenum nitride, show that it can be an excellent potential substitute for hydrotreating catalysis. But till to this date, the majority of applied catalysis research for this system has been conducted over Mo2N. This proposed research is intended to explore the activity of recently developed lamellar MoN sheets for catalytic hydrogendenitrogenation (HDN) associated with larger organics, relevant to oil refinery applications (i.e. pyridine and carbazole conversion).

Delta phase MoN (δ-MoN) is preferable for this process due to the expected weakening of the Mo-N bonds within MoN relative to Mo2N due to higher nitrogen coverage in MoN and its catalytic activity is expected to be enhanced when lamellar sheets of MoN are used due to the higher surface area to volume ratio. In addition to δ-MoN, we will explore and compare the catalytic activity of different forms of molybdenum nitrides.

The lamellar sheet of the δ-MoN will be grown by using method established elsewhere and the conventional surface science techniques, like scanning-tunneling microscopy (STM), atomic force microscopy (AFM), and kelvin probe force microscopy (KPFM) will be used to make the molecularly, atomically and in some cases sub-atomically localized measurements of surface structures.

**SS-TuP11 Infrared Analysis of Competitive Surface Adsorption in Superconformal Chemical Vapor Deposition**, ***Zhejun Zhang***, *E. Mohimi, T.K. Talukdar, G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign

A major challenge in nanoscale device fabrication is to fill a deep via or trench with material without leaving a low density ‘seam’ along the centerline. We previously demonstrated two variants of low temperature chemical vapor deposition (CVD) that afford *superconformal* coating, in which film growth is faster deep in the feature that near to the opening. This affords a ‘V’ shaped coating profile, and as deposition proceeds, the apex of the V moves upwards until the feature is completely filled. Our first method, suitable for the growth of metallic films such as $CrB_2$, involves the use of a highly reactive inhibitor, such as H atoms, in conjunction with the CVD precursor to suppress the growth rate in the upper portion of the feature. Our second method, suitable for dielectric deposition such as MgO, takes advantage of the intrinsic competition between two reactants, such as the precursor and water, on the film growth surface for adsorption sites. In both cases, the kinetic results are successfully modeled using Langmuir-Hinshelwood (LH) adsorption theory in combination with molecular transport of the reactants inside the feature.

In this interpretation, the suppression of film growth rate corresponds to a situation in which a significant fraction of the surface binding sites are occupied (blocked) by a species that does not lead to film growth, either the inhibitor in the first case or an excess of one reactant in the second case. However, we have not had any direct proof of this assumed mechanism. To obtain direct insight, we have implemented reflection FTIR spectroscopy in order to measure the surface coverage in adsorbates in real time during film growth. This is very challenging experimentally, however, the use of a thin dielectric on metal substrate at high angle of incidence provides enough signal enhancement in p-polarization to observe sub-monolayer coverages. In addition, the intrinsic cancellation of the absorption signal in s-polarization means that the contribution of gas phase absorption can be cancelled out by subtraction of the p and s signals.

We report the absorption competition for surface sites for the growth of MgO and $HfO_2$ by low temperature CVD, and we compare the measurements with the range of values estimated from LH theory in view of the molecular fluxes to the surface and the measured film growth rates. As expected, the data reveal surprises such as a low total surface coverage in adsorbates even under competitive kinetics, indicating that the density of binding sites is significantly smaller than the geometric density of sites for these oxides.

**SS-TuP15 Universal Calibration of Computationally Predicted N 1s Binding Energies for Interpretation of XPS Experimental Measurements**, ***Jing Zhao****, *A.V. Teplyakov*, University of Delaware

An independent approach was obtained to calibrate simulated N 1s core level energies by density functional theory to interpret XPS experimental measurements. In this work, we compare the application of two basis sets, LANL2DZ and 6-311G+(d,p) and B3LYP functional and analyse the correlation factors contributing to theoretical with experimental results. The correlation is first examined with the known nitrogen-containing functional groups on well-characterized and well-understood organic monolayers and then applied to a number of nitrogen-containing chemical systems where the nature of the chemical environment of nitrogen atoms had only been proposed based on a number of analytical techniques. Based on this independent calibration approach, a high degree of correlation is obtained and the basic strategies for comparing computationally predicted and experimentally obtained values are proposed.

**SS-TuP18 Vibrational Spectroscopy of Hydrogen Sulfide Adsorbed on Metallic W (100) and Oxygen Adsorbed W (100)**, ***Joel Langford***, *A.D. Babore, J.C. Hemminger*, University of California Irvine

High resolution electron energy loss spectroscopy, Auger electron spectroscopy, and temperature-programmed desorption has been used to study hydrogen sulfide adsorbed on two systems; metallic W (100) and oxygen adsorbed W (100). At exposure temperatures of 150 K hydrogen sulfide dissociates on both systems. However, for metallic W (100) and oxygen adsorbed W (100) the dissociation products are different. On metallic W (100) hydrogen sulfide dissociates to form W-SH and W-H. On oxygen adsorbed W (100) hydrogen sulfide dissociates to produce a combination of W-SH, W-OH, and W-H. These species were confirmed with both $D_2O$ and $D_2S$ experiments. When metallic W (100) is annealed SH groups recombine to desorb as molecular hydrogen leaving behind the W-S species. Therefore, adsorption of hydrogen sulfide on W (100) is irreversible. Both the vibrational spectroscopy and thermal desorption lack evidence of molecularly adsorbed $H_2S$. The desorption peak for molecular $H_2S$ is therefore below the 150 K exposure temperature. On oxygen adsorbed W (100) both water and hydrogen desorption is observed. The intensity ratio of

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* **Morton S. Traum Award Finalist**

W-OH to W-SH vibrational modes and the water to hydrogen desorption ratio as a function of surface oxygen to tungsten was measured. Both the intensity ratio of W-OH to W-SH vibrational modes and water to hydrogen desorption peak is proportional to the oxygen concentration. A descriptive interpretation of hydrogen sulfide W (100) chemistry will be provided in this talk

**SS-TuP19 Lubricity of Gold Nanocrystals on Graphene Measured using Quartz Crystal Microbalance**, *M.S. Lodge*, University of Central Florida, *C. Tang*, University of California Merced, ***Brandon Blue***, University of Central Florida, *W. Hubbard*, University of California at Los Angeles, *A. Martini*, University of California Merced, *B. Dawson, M. Ishigami*, University of Central Florida

Recent simulations [Guerra et al, Nature Materials, 9, 634 (2010)] have predicted that, at high sliding speeds, gold nanocrystals slide with vanishing friction on graphite. Unlike structural or super-lubricity observed previously in nanotribology experiments, the predicted reduction of friction by two orders of magnitude was found to be independent of the commensurability between the two sliding surfaces. As such, the predicted phenomenon, named ballistic nanofriction, is novel and different from any phenomena previously observed in nanotribology.

In this talk, we present experimental evidence of ballistic nanofriction for gold nanocrystals deposited onto graphene-coated quartz crystal microbalances (QCMs) under UHV. Lubricity exceeding ballistic nanofriction is observed down to surface velocities of 4.7 cm/sec: much lower than expected from the work of Guerra et al. The observed drag coefficients are ~$8.65\times10^{-14}$ kg/s. This is significantly smaller than the theoretically-predicted value of $2.0\times10^{-13}$ kg/s, and suggests a much lower interaction strength between graphene and gold nanocrystals than previously assumed in contemporary theoretical models of gold nanocrystals on graphite.

Acknowledgements: This work is based upon research supported by the National Science Foundation under Grant No. 0955625 (MLS, BTB, BDD and MI) and Grant No. CMMI-1265594 (CT and AM). BDD and MI were also supported by the Intelligence Community Postdoctoral Fellowship.

**SS-TuP20 Controllable Synthesis of Ru/Pt Core Shell Nanoparticles with Bi-functional Interfaces towards PROX Reactions**, ***Yun Lang***, *J.Q. Yang, K. Cao, M. Gong, B. Shan, R. Chen*, Huazhong University of Science and Technology, PR China

Bimetallic nanoparticles (NPs) have attracted great attention due to their unique properties for catalytic applications. Compared with the physical mixture of monometallic NPs or alloyed bimetallic NPs, the formation of core shell structure could further enhance the activity, selectivity and stability. Synthesizing core shell NPs with well controlled shell thickness and composition is of great importance in optimizing their reactivity. Here we report synthesis of Ru/Pt core shell NPs using area-selective ALD techniques. The catalytic performance towards preferential oxidation of CO under excess $H_2$ (PROX) reaction is studied with different Pt shell thickness. The catalytic activity of hybrid nanostructure can be tuned continuously with shell thickness originated from electron structure modification. Utilizing the lattice mismatch between Pt(111)/Ru(101), Pt(111) layer can be selectively deposited on Ru (001) facet while leaving Ru (101) uncovered. The exposure facets demonstrate two functions in PROX reaction, Pt(111) on Ru(001) decrease CO reaction barrier and Ru (101) increase active oxygen adsorption and dissociation. Both activity and selectivity towards PROX reaction have been enhanced compared with fully covered Ru/Pt core shell nanoparticles or their alloy.

**SS-TuP21 Corrosion Resistance of Yttrium Trifluoride (YF3) and Yttrium Oxyfluoride (YOF) used in Plasma Process Chamber**, ***Yoshinobu Shiba***, *A. Teramoto, T. Goto*, Tohoku university, Japan, *Y. Kishi*, Nippon Yttrium Co., Ltd, Japan, *Y. Shirai, S. Sugawa*, Tohoku university, Japan

Chemically stable materials that have corrosion resistance from reactive species enhanced by plasma have been required for an inner wall of semiconductor process chambers. Although the materials with low formation enthalpy (such as aluminum oxide ($Al_2O_3$) and yttrium oxide ($Y_2O_3$)) have been widely used for the protect material, it was revealed that yttrium oxyfluoride (YOF) was much stable than $Y_2O_3$ against the reactive species. [1] In this research, we compared the chemical stability of Yttrium trifluoride ($YF_3$) and that of YOF. The enthalpy of formation of $YF_3$ (-1719 kJ/mol) is close to $Y_2O_3$'s (-1905 kJ/mol), and the enthalpy of formation of one metal-fluorine bond of $YF_3$ (-573 kJ/mol) is smaller than that of one metal-oxygen bond of $Y_2O_3$ (318 kJ/mol). $YF_3$ films and YOF films were exposed to $N_2$/Ar, $H_2$/Ar, $NH_3$/Ar, $NF_3$/Ar, and $O_2$/Ar plasmas using microwave-excited surface-wave high-density plasma equipment [2], and investigated their corrosion resistance. After plasma-irradiation, the $YF_3$ film's surfaces were damaged, and the fluorine content in $YF_3$ decreased in all condition. In contrast, the YOF's surfaces were not changed by these plasmas. These indicate that the YOF is much stable against the plasma bombardment than the $YF_3$.

[1] Shiba et al. J. Vac. Sci. Technol. A 35, 021405 (2017)

[2] T. Ohmi, et al. J. Phys. D: Appl. Phys., 39, R1 (2006)

## Vacuum Technology Division
## Room: Central Hall - Session VT-TuP

## Vacuum Technology Poster (and Student Poster Competition)

**Moderators:** James Fedchak, NIST, Yevgeniy Lushtak, SAES Getters USA

**VT-TuP1 Ion-Cathode Bombardment in a DC Deuterium Glow Discharge for High-Density Deuterium Cluster Formation in Metals**, ***Erik Ziehm***, *G.H. Miley*, University of Illinois at Urbana-Champaign

A deuterium glow discharge is modeled to obtain angular and energy distributions of incident ions on the cathode vs plasma conditions. The model uses a DC Discharge module in COMSOL Multiphysics® [1] coupled to a Particle Tracing module while utilizing Townsend coefficients for prominent reactions derived from a Boltzmann Two-Term Approximation. Care is taken to use appropriate ionization and dissociation reaction cross sections for deuterium as these values present isotopic differences. The model is benchmarked by Langmuir probe measurements of the electron energy distribution along the cathode dark space and negative glow regions. This model is then used to determine the effects of ion incident energies and dose on the creation of the high-density clusters of deuterium atoms beneath the cathode surface layer. Temperature Desorption Spectroscopy (TDS) complimented with X-Ray Diffraction (XRD) is employed to determine the clusters' trapping energies and densities.

**VT-TuP2 Low-cost Device Fabrication and Vacuum Packaging for Energy Efficient Field Emission Lighting**, ***Sushma Shrinivasan***, *C.E. Hunt*, University of California - Davis

With the growing emphasis on climate change and global warming and the resulting need to cut down energy usage, energy-efficient lighting technologies that resemble day light spectrum and do not present health hazards are extremely attractive. Field emission lamps (FELs) have been presented as a viable alternative to existing lighting technologies with several advantages including (i) spectrum similar to daylight (ii) environment-friendly (iii) no health hazards to name a few. In this regard, the primary goal of this poster is to present a low-cost, simple device fabrication technique for a typical FEL. The FEL device consists of a base plate, face plate and side-wall (all made out of glass). The glass package is built by attaching the various components using ultra high vacuum epoxy. The base plate and face plate comprise of the cathode (reticulated vitreous carbon) and anode (aluminum coating) respectively with the face plate additionally comprising of a phospor coating. The exhaust tube for the device is located on the side-wall. The device is then attached to a turbomolecular pump and pumped down to vacuum levels of 1E-6 Torr. This level of vacuum is shown to activate the barium getter that is attached to the baseplate before the device packaging. The activation of the barium getter is performed using an in-house induction coil and a radio frequency generator operated at a frequency of 300 kHz. The packaged device when combined with a high voltage DC power supply is anticipated to lead to a low-cost energy efficient lighting option that has a spectrum similar to incandescent lamps with an energy consumption comparable to compact fluorescent lamps.

**VT-TuP3 High Precision Measurement Of Tube Conductance From Pressure Decay Curve**, ***Tim Verbovšek***, *B. Šetina Batič, J. Šetina*, Institute of Metals and Technology, Slovenia

A unique vacuum system for precise measurement of gas throughput through a tube connecting a vacuum chamber and a pump was constructed. A conductance of a duct between the pump and the vacuum chamber determines the rate of pressure decay $p=p(t)$ when nonadsorbing gas is pumped. If gas back-streaming from the pump through the duct is negligible, and gas temperature in the duct is the same as in the chamber, the conductance $C$ of the duct can be calculated from the time derivative of the logarithm of the pressure decay by $C=V\times d(\ln(p))/dt$, where $V$ is volume of the chamber. The simplicity of this equation is also a basis for a very high precision of such measurement. Uncertainties which have to be considered are related to the volume of the chamber and deviations from isothermal conditions. Since logarithm of the measured $p(t)$ curve is used to calculate conductance, any correction factor of the vacuum gauge cancels out. Moreover, different sensitivity of the vacuum gauge for different gases is totally unimportant, so only random noise of the measured pressure contributes to the uncertainty.

Estimated relative uncertainty of measured conductance is less than 0.3%. Reproducibility (with volume *V* unchanged) is even less than 0.2%.

Very high precision of this method enables studies of the influence of gas-surface interaction on the tube conductance in molecular regime. Any changes of tangential momentum accommodation coefficient reflect in variation of the tube conductance. We will present results of measurements of conductance of a long stainless steel tube with inner diameter of 7.76 mm for initial state and after different treatments (all at 300 °C for 24 h): exposure to $O_2$ at 0.1 Pa, vacuum bake, and exposure to $H_2$ at 0.1 Pa. Conductance was measured for gasses He, Ne, Ar, Kr, $CH_4$ and $N_2$ in the range of Knudsen numbers from 0.01 to 1000. Variations of molecular scattering on the tube surface resulted in changes of tube conductance of more than 10 % for He, while for $N_2$ and $CH_4$ the observed changes were less than 2 %.

### VT-TuP4 Using a High Vacuum Equipment Trainer (HVET) System for Hands-on Learning, ***Del Smith***, *N. Louwagie*, Normandale Community College

In keeping with the theme of the 2017 Symposium, "Surfaces, Interfaces and Materials: A New Vision," this paper will discuss the experiences of Normandale Community College (Bloomington, Minn.) instructors offering academic courses in vacuum and thin film technology via a telepresence interface. We believe this new model, which brings together on-campus and remote learners in real time, is a positive direction for technical education. Over the past two years, several organizations throughout the U.S. have enrolled their employees and students in courses, which emphasize hands-on learning with a vacuum trainer system.

Normandale staff in the Vacuum and Thin Film Technology Program, with input from senior technicians from several Minnesota-based industries, designed a High Vacuum Equipment Trainer (HVET) system to use in the classroom. The HVET system has $5x10^{-6}$Torr base pressure capability and supports demonstrations of vacuum technology operations such as gauging, gas sensitivity, leak testing, RGA analysis, and plasma generation. Students use the HVET system to practice pumpdown sequences, pumpdown curves, rates of rise, and conductance in a lab environment. There are four copies of the HVET, which can be disassembled and shipped to participating sites; students assemble the HVET system as part of their initial learning experience.

The telepresence classroom at Normandale was designed with a combination of high-performance audio and video feeds and multiple monitors to show close-ups of lab experiments and to allow the instructor to respond to nonverbal cues from remote students. Normandale offers an AAS degree in Vacuum and Thin Film Technology. Two courses from this program are available via telepresence: Intro to Vacuum Tech and Vacuum Analysis and Troubleshooting. Eventually, two more courses will be brought online: Thin Film Deposition; and, Foundations in Vacuum Technology, which will teach chemistry and math concepts in the context of vacuum science. Students will be able to complete these courses in a year, via telepresence, earning a Vacuum Technology Certificate and 12 academic credits, which are applicable towards the AAS degree. This paper will discuss how the trainer systems and telepresence provide remote students with access to formal education in vacuum and thin film technology. (This work was made possible in part by a grant from the National Science Foundation: DUE #1400408.)

### VT-TuP5 Advanced Metal Sealing Solutions for Critical Industry Applications, ***Ryan McCall***, Technetics Group

As operating conditions in many critical industries, such as vacuum and semiconductor, continue to face increasingly extreme temperatures and pressures, sealing technologies are facing challenges that cannot be met with traditional materials and methods. Additionally, there are growing pressures to ensure the protection of the environment remains a top priority for companies and that they are consistently meeting the strict requirements associated with international regulations. More and more manufacturers are turning to metal seals as their solution of choice as today's industry requirements are becoming more and more stringent.

Because of these stringent requirements, metal seals designed for use in modern sealing applications must be resilient to the extreme temperatures and pressures that they are exposed to in a number of harsh environments. Seal designs must also allow for bi-direction flow, be suitable for axial and radial applications, provide a long sealing life, be resistant to corrosion, be able to remain as leak tight as possible under semi-dynamic motions and account for thermal expansions.

This presentation will explain the factors to consider when selecting a metal sealing solution and what types of seal designs (spring-energized, O-rings, C-rings, E-rings, etc) are best suited for each given aspect of a critical industry application. The factors that will be discussed in the presentation will include but are not limited to seating load, seal function, seal material and thickness, required leak rate, coatings, controlled compression and surface finish. Additionally, the specific applications where metal seals are most suited and why will also be discussed.

### VT-TuP6 Development of the Residual Gas Analysis for Large Air Tight Packages, ***Yusuke Nishikawa***, Advanced Technology R&D Center Mitsubishi Electric Corp., Japan, *M. Kinugawa*, Advanced Technology R&D Center Mitsubishi Electric Corp.

A hollow airtight packaging structure is used for electric / electronic parts (e.g. lamps, high frequency devices, etc.) to improve reliability and securing characteristics. It is crucial to know the variety and amount of impurities in the structure's internal gas, which adversely affects said properties. We have developed a gas analysis technique for small parts with an internal volume of 1 cm3 or less [1].

In the case of small package devices, it is possible to break it in a vacuum chamber and analyze the gas inside. However, when analyzing residual gas with a large package, it is very difficult to prepare a larger chamber and break the sample. Furthermore, if the surface area in the package is large, the influence of desorption of adsorbed molecules cannot be ignored. It is difficult to accurately measure the pressure of residual gas.

In this study, we present a new technique for analyzing gas in sealing devices that can be flexibly applied and can minimize the influence on the state of the residual gas composition even for various large samples.

The testing apparatus consists of a gas sampling chamber and an analysis chamber, with both connected to a vacuum valve and an exchangeable orifice. The analysis chamber has a quadrupole mass spectrometer and is exhausted continuously by a turbomolecular pump. The gas sampling chamber has a perforator, a vacuum gauge, and an additional pumping system. The volume of the gas sampling chamber is sufficiently small relative to the volume of the sample. The package sample is connected directly to the connection port of the gas sampling chamber. By using a small gas sampling chamber, an external connection of the sample, and a variable orifice, this technique can be flexibly applied to various large samples.

We measured the temperature of the internal pressure of a certain package sample. As a result, we found that the pressure increase was five times higher than when considering by the ideal gas law and ion intensity of water was increased. We estimated them as the adsorption and desorption levels of gas on the surface of the internal components.

To further advance this technique, we found that it is important to know the influence of gas adsorption and desorption inside the package. We will research the gas adsorption and desorption for the component parts affecting residual gas partial pressure.

[1] M. Kinugawa, et al.: Mitsubishi Denki giho Vol. 81 No. 3 231 (2007).

### VT-TuP7 ARIEL RIB Transport line Vacuum System, ***Geoffrey Hodgson***, TRIUMF, Canada

The vacuum system of the Radioactive Isotope Beam (RIB) transport line is part of the Advanced Rare IsotopE Laboratory (ARIEL) at TRIUMF. This beam line will accept three simultaneous RIBs and transmit two of them to low energy experimental facilities and one to further accelerators. The RIBs will consist of ions of exotic radioactive species with masses ranging from 6 to 238 amu and energies from 10 to 60 keV. RIBs will be extracted from two new ARIEL target stations and one of two existing ISAC target stations. In ISAC, and one of the ARIEL target stations, targets materials ranging from metals, oxides, carbides to actinide compounds are irradiate by 50kW, 500 MeV protons from TRIUMF's main cyclotron. The second ARIEL target will make use of 100 kW, 35 to 50 MeV electron beam which is converted to high-energy gamma rays in a thin layer of gold. These gamma rays are used for photodisintegration of beryllium oxide or photo photofission of uranium carbide. The beam line will be built on two floors. The lower floor will contain Medium and High Resolution mass Spectrometers (MRS and HRS) having 1:5,000 and 1:20,000 resolution, respectively. The upper floor will contain charge breeding equipment to provide a typical mass to charge ratio of 7 to allow further acceleration of heavier isotopes. The design pressure is $3\cdot 10^{-8}$ Torr for singly charged beams and $1\cdot 10^{-8}$ Torr for highly charged ion beams based on beam loss calculations. The system will use turbo pumps and scroll pumps to achieve the vacuum. Individual components of beam line and beam steering equipment were tested to determine their conductance in molecular flow, and the model of the vacuum profile was created. A 14.5 m prototype section of beam line was built and used to validate the profile model. The beam line is divided into isolable sections, and each section will have a standard vacuum pumping station to facilitate controls and interlocks.

### VT-TuP8 Operational Regime of 2 million L/s Cryobox Pump on Tri Alpha Energy's C2W Machine, ***Ernesto Barraza-Valdez***, *A. Van Drie*, Tri Alpha Energy, Inc.

Tri Alpha Energy requires a large pumping speed of approximately 2 million L/s for hydrogen and 1.5 million L/s for deuterium in each of the four divertors (22,000 L) on C2W. To accomplish this TAE has developed a liquid nitrogen cooled, titanium getter pump. The experimental pump speed was tested for a variety of parameters including purity of titanium (99.995% and 99.97% Ti), various temperatures, and saturation. Purity of titanium showed no effect on the pump speed but there was a clear correlation with the temperature and saturation. With this, TAE had discovered a regime of operation during plasma shots in C2W.

## 2D Materials Focus Topic
## Room: 15 - Session 2D+EM+SS+TF-WeM

### 2D Materials Growth and Fabrication
**Moderator:** Aleksandra Radenovic, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

8:00am **2D+EM+SS+TF-WeM1 Chemical Bath Deposition of Phase Selective $MoS_2$ on Templated Surfaces**, ***Jenny Hedlund***, *A.V. Walker*, University of Texas at Dallas

Transition metal dichalcogenides (TMDs) have a wide range of physical properties, and consequently have applications in nanoelectronics and biosensors. While TMD materials have been well studied, a simple method for two-dimensional large area thin film deposition of these materials has yet to be achieved. Chemical bath deposition (CBD) is a robust method by which to grow uniform thin films, and offers many advantages over other techniques including low deposition temperatures (≤ 50°C), synthetic flexibility, and it is inexpensive. In this work, CBD is used to deposit large-area ultra-thin molybdenum disulfide ($MoS_2$), a group VI TMD, and the resulting deposits are investigated by scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), Raman spectroscopy and time-of-flight secondary ion mass spectrometry (TOF SIMS). These TMDs are most commonly found to possess trigonal prismatic crystalline structure (2H phase) and therefore are semiconductors. Although less widely studied, TMDs can also possess octahedral crystallinity to form the 1T phase. The 1T phase exhibits different properties to the 2H phase, and has applications in sensing, metal contacts and catalysis. By using substrates that mimic the TMD crystalline structure for deposition we have shown that $MoS_2$ can be deposited with large-area crystallites observed. SEM images of deposition performed on highly oriented pyrolytic graphite show large area flakes, ~100 µm in diameter. Smooth thin films were also deposited on sapphire, and functionalized self-assembled monolayers (SAMs). XPS results show that Mo 3d and S 2s peaks are present in the expected positions and ratios. We further demonstrate that the deposited $MoS_2$ phase is likely determined by the surface chemistry of the substrate. Using Raman spectroscopy measurements, the thickness and phase of the film are elucidated. CBD of $MoS_2$ was further characterized using TOF SIMS to elucidate the reaction mechanisms as well as the stability of the deposited film.

8:20am **2D+EM+SS+TF-WeM2 Atomic Layer and Metalorganic Chemical Vapor Deposition of $MoS_2$ and $WS_2$ from bis(tert-butylimido)-bis(dialkylamido) Compounds**, ***Berc Kalanyan***, *J.E. Maslar, W.A. Kimes, B.A. Sperling,* NIST, *R. Kanjolia,* EMD Performance Materials

Layered 2D transition-metal dichalcogenides (TMDs) are finding use in nanoelectronic and optoelectronic applications due to their thickness-dependent optical and electrical properties. Scalable fabrication of TMD-based devices requires vapor-phase deposition routes that can produce continuous and uniform films with sub-nanometer thickness control. Atomic layer deposition (ALD) is a desirable route for the synthesis of 2D TMDs and heterostructures due to digital thickness control achieved by sequential self-limiting surface chemistry. However, since ALD conditions are only met at relatively low deposition temperatures, most ALD films are amorphous. Some consider this a useful feature of ALD, since film growth rate and structural development can be decoupled by separating the deposition and crystallization steps. In contrast, metalorganic chemical vapor deposition (MOCVD) enables direct growth of crystalline films, but requires careful process control and precursor selection to achieve the required level of thickness control. The tradeoffs between direct CVD growth and post-sufurization and annealing of amorphous/metallic films is the focus of this work.

In this paper, we present a comparison of process characteristics and film properties, including growth rate, thickness, morphology, composition, and crystallinity, as a function of two deposition routes: ALD and MOCVD. We deposited thin films using $(N^tBu)_2(NMe_2)_2M$ and 1-propanethiol, where M={Mo,W}, at wafer temperatures of 200°C to 400°C for ALD and 400°C to 900°C for pulsed MOCVD on $SiO_2$/Si substrates. Precursor saturation conditions were evaluated using in situ infrared flow measurements and ex situ X-ray photoelectron spectroscopy. As-deposited and sulfur-annealed films were further evaluated using X-ray diffraction, optical spectroscopies, and microscopy. As-grown ALD films were amorphous and included a mixture of a sulfide and a conductive phase, likely a nitride. Below 300°C, deposition was limited to a thin surface oxide. Higher temperatures resulted in higher growth rates, which also introduced a weak CVD component to the growth. Deposition rates were <1.0 Å/cycle at 350°C. As-deposited films were successfully annealed to 2H-$MoS_2$ under a sulfur atmosphere, which also removed residual nitrogen. As-grown MOCVD films were polycrystalline 2H-$MoS_2$ at 600°C. Pulsed injections of precursor enabled Å-level control over aggregate film thickness. For both processes, wafer-scale growth and uniformity in a perpendicular flow reactor were demonstrated on 50 mm substrates. We will also present process characteristics for the analogous $WS_2$ route and discuss initial data from $MoS_2$/$WS_2$ nanolaminates.

8:40am **2D+EM+SS+TF-WeM3 Epitaxial Growth of Atomically Thin Transition Metal Dichalcogenides and their Electronic Structures**, ***Sung-Kwan Mo***, Lawrence Berkeley National Laboratory **INVITED**

Transition metal dichalcogenides (TMDCs) is a versatile material platform with a variety of electrical, optical, and topological properties that can be controlled through thickness, strain, field, and other perturbations. In this talk, I will first discuss the growth of atomically-thin TMDC films, such as $MoSe_2$, $WSe_2$, $WTe_2$, $NbSe_2$, and $TaSe_2$, with a layer-by-layer thickness control, using molecular beam epitaxy. Then, I will present how we investigate the electronic structures of these films using angle-resolved photoemission spectroscopy and scanning tunneling microscopy.

9:20am **2D+EM+SS+TF-WeM5 Terminations and Treatments of Silicon Carbide Surfaces to Promote Epitaxial Hexagonal Boron Nitride Deposition by Chemical Beam Epitaxy**, ***Daniel Pennachio***, *N.S. Wilson, A.P. McFadden, T. Brown-Heft,* University of California at Santa Barbara, *K.M. Daniels, R.L. Myers-Ward, D.K. Gaskill, C.R. Eddy, Jr.,* U.S. Naval Research Laboratory, *C.J. Palmstrøm*, University of California at Santa Barbara

This work examines the epitaxial deposition of single-crystal hexagonal boron nitride (h-BN) on silicon carbide substrates through the use of surface treatments which promote suitable nucleation and growth. Silicon carbide, 6H-SiC(0001), was chosen as a candidate substrate due to its market availability, high crystalline quality, temperature stability, and potential coincident lattice match to h-BN. Boron nitride was deposited in ultra-high vacuum (UHV) environments by chemical beam epitaxy (CBE) on SiC substrates through thermal decomposition of borazine at high temperatures. Different SiC surface reconstructions reached through exposure to elemental silicon and subsequent *in-vacuo* annealing were examined for their effect on h-BN nucleation and epitaxial arrangement. Along with reconstructions produced through UHV annealing, CVD-grown epitaxial graphene on 4H-SiC was also utilized as a growth surface. Growth past full single atomic layer coverage of $sp^2$-bonded material (either h-BN deposited layers or graphene substrates) proved difficult with the accessible temperature range and precursor flux. Various surface treatment approaches were investigated to promote additional layer growth.

Deposited h-BN films on the SiC reconstructed surfaces were found to be near-stoichiometric and of single- to few-atomic layer thickness, as determined by *in-situ* x-ray photoelectron spectroscopy (XPS) B1s:N1s peak area ratios and substrate peak attenuation. Progression of *in-situ* reflection high-energy electron diffraction (RHEED) during h-BN deposition provides evidence of a difference in film nucleation between the Si-rich (3x3) and the C-rich SiC surface reconstructions: while the (3x3) reconstruction quickly transitioned to a (1x1) reconstruction upon precursor dosing, the C-rich reconstruction persisted despite thicker depositions. XPS of the C-rich surface showed a higher binding energy shoulder of the C1s peak, indicative of $sp^2$-hybridized bonding in a graphene-like buffer layer at the surface. Triangular nuclei seen by scanning electron microscopy after deposition on the C-rich SiC surface suggests epitaxial arrangement to this buffer layer. *In-situ* scanning probe microscopy and *ex-situ* transmission electron microscopy were performed to acquire additional information on film morphology. The influence of different surface treatments for increasing the thickness of h-BN growth will be presented.

9:40am **2D+EM+SS+TF-WeM6 Photo-Chemical Modification of Monolayer Transition Metal Dichalcogenides**, ***Tariq Afaneh***, *P.K. Sahoo, H.R. Gutierrez,* University of South Florida

Fabrication of in-plane 2D heterostructures is a crucial step to advance in the development of a truly 2D optoelectronics. Different approaches have been attempted, including in situ sequential growth of two different materials and post-growth modification of the chemical composition in a 2D monolayer. In this work, we studied a post-growth technique that exploits the radiation-matter interaction under a controlled atmosphere. Using a homemade sealed mini-chamber with a quartz optical viewport, a laser beam (532 nm) was focused onto the sample, consisting on $MoSe_2$ or $WSe_2$, while keeping a reactive sulfur-rich atmosphere within the chamber. The spatially localized photo-chemical conversion was in situ monitored by mapping the temporal evolution of the Raman active modes. The process can be tuned thereby choosing appropriate laser power, exposure time, and reactive gas environment. The complete or partial conversion was further confirmed by collecting the photoluminescence spectra at the desired exposed sites. The time-dependent intensities of the Raman peaks were fitted to exponentially decaying functions. Depending on the reaction parameters, two different processes with distinct time constants can be identified. The following mechanisms for the photo-conversion are proposed: (i) creation of Se vacancies in the TMD materials due to the energy absorbed from the laser radiation, (ii) cracking of sulfur containing molecules from the gas environment and subsequent incorporation of the sulfur atoms into the Se vacancy sites. The optimization of this process will allow to develop techniques based on photo-induced chemical reactions for local doping, alloying and the fabrication of in-plane TMD heterostructure.

11:00am **2D+EM+SS+TF-WeM10 Bottom-up synthesis of Graphene Nanomembranes with Tunable Porosity**, ***Christof Neumann***, Friedrich Schiller University Jena, Germany, *M. Füser*, Goethe University Frankfurt, Germany, *M. Mohn*, Ulm University, Germany, *D. Kaiser*, Friedrich Schiller University Jena, Germany, *A. Gölzhäuser*, Bielefeld University, Germany, *U. Kaiser*, Ulm University, Germany, *A. Terfort*, Goethe University Frankfurt, Germany, *A. Turchanin*, Friedrich Schiller University Jena, Germany

The potential of atomically thin materials like graphene or carbon nanomembranes (CNMs) [1] for separation or ultrafiltration technologies is based on their negligible thicknesses enabling the ballistic transport of atoms and molecules through the nanomembranes. For such implementations, large scale production of perforated nanomembranes with well-defined sizes of nanopores has to be established. Here we present a scalable method to produce atomically thin graphene nanomembranes with tunable porosity using aromatic self-assembled monolayers (SAMs) as molecular precursors. We employ N-containing 4-(1H-pyrrol-1-yl)thiophenol, 4-(2,5-dimethyl-1H-pyrrol-1-yl)thiophenol and 4-(pyrimidin-2-yl)phenylthiol SAMs on polycrystalline copper foils to convert them into CNMs via low energy electron irradiation induced crosslinking and then to pyrolyze CNMs into nanoporous graphene sheets in vacuum. We characterize the formed supported and suspended graphene nanosheets by different complementary spectroscopy and microscopy techniques including X-ray photoelectron (XPS) and Raman spectroscopy, atomic force (AFM), helium ion (HIM) and high-resolution transmission electron microscopy (HRTEM) as well as by electric transport measurements. We demonstrate that the pore size and the graphene crystallinity can be adjusted by the production parameters and discuss the mechanisms.

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11:20am **2D+EM+SS+TF-WeM11 Cu Single Crystal Substrates for Growth of CVD Graphene**, ***Tyler Mowll***, University at Albany, SUNY, *Z.R. Robinson*, SUNY Brockport, *C.A. Ventrice, Jr.*, SUNY Polytechnic Institute

To provide a systematic study of the CVD graphene growth process, a study of the growth of graphene on single crystal Cu substrates, with terminations along the (100), (110), and (111) planes, was performed. Synthesis was performed in an ultra-high vacuum (UHV) chamber using a modified setup to allow growth at pressures as high as 1 Torr. Ethylene was used as the precursor gas. To control Cu sublimation at the elevated growth temperatures, an Ar overpressure was used. This arrangement allowed for the preparation of clean Cu surfaces by sputtering and annealing the Cu crystals in UHV, followed by graphene growth at low pressure, and in-situ analysis with low energy electron diffraction. It was found that surface termination plays a strong role in the rotational alignment of the nucleating graphene grains and the decomposition rate of the ethylene. It was observed that single-domain epitaxy is possible on Cu(111) when the ethylene pressure is 5 mTorr or less. However, growth on both Cu(100) and Cu(110) result in a minimum of two domains. In addition, ex-situ EELS is currently being performed on well-ordered epitaxial graphene films grown on Cu(111) and Cu(100) to determine the effect of the graphene-Cu interaction on the electronic properties of the graphene.

11:40am **2D+EM+SS+TF-WeM12 Paper and Circuits, only Atoms Thick**, ***Jiwoong Park***, University of Chicago **INVITED**

2D layered materials are like paper: they can be colored, stitched, stacked, and folded to form integrated devices with atomic thickness. In this talk, I will discuss how different 2D materials can be grown with distinct electrical and optical properties (coloring), how they can be connected laterally to form pattered circuits (stitching), and how their properties can be controlled by the interlayer rotation (twisting). We will then discuss how these atomically thin papers and circuits can be folded to generate active 3D systems.

## 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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[2] M. Benguerba, et. al. Nucl. Instrum. Meth. B 62 (1991) pp. 8-22.

[3] Kollmer, F. (2004): Applied Surface Science 231-232, pp. 153–158

[4] Kollmer, F. et. al. (2013) Surface and Interface Analysis 45 (1), pp. 312–314

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

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* **ASSD Peter Sherwood Award**

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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2) E. Niehus, T. Grehl, in: J.C. Vickerman, D. Briggs (Eds.), ToF-SIMS, IMPublications, Chichester, West Sussex, UK, 2001, p. 753.

3) J. Brison and L. Houssiau, *Surf. Interface Anal*. 2006; 38: 1715-1719.

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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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## Biomaterial Interfaces Division
## Room: 12 - Session BI+NS-WeM

## Biomaterials and Nanomaterials Fabrication & In Honor of Dave Castner's 65th Birthday: Multitechnique Bio-Surface Characterization I

**Moderator:** Caitlin Howell, University of Maine

8:00am **BI+NS-WeM1 Plasma-Enhanced Chemical Vapor Deposition of an Antibacterial Coating from an Essential Oil-Derived Precursor**, ***Michelle Mann***, *E.R. Fisher*, Colorado State University

Polymeric constructs, such as filtration membranes for water treatment and nanocomposite scaffolds for wound healing and drug release, are often chosen for their ideal bulk properties (e.g., porosity, mechanical strength, and chemical inertness). Challenges faced when using such materials in aqueous settings, however, include their hydrophobicity and propensity for bacterial attachment, leading to biofilm formation and degradation of material performance. Modifying the surface of the constructs while simultaneously maintaining the bulk properties offers both the possibility of addressing these limitations and the potential for creating new advanced materials. Plasma processing is a valuable tool often used to improve material wettability and deposit antifouling coatings. Here, plasma-enhanced chemical vapor deposition is used to deposit films from eucalyptol (1,8-cineole), an antibacterial precursor derived from tea tree oil. Although the antibacterial properties of eucalyptol are supported by numerous clinical trials, it is unknown to what extent the monomer structure and biocidal capabilities are maintained in plasma polymerized films. Thus, we have explored the properties of the eucalyptol-based films as a function of plasma parameters (e.g., power, pressure). Surface analyses (contact angle goniometry, X-ray photoelectron spectroscopy, scanning electron microscopy, and optical profilometry) reveal film wettability directly correlates to precursor pressure, with water contact angles ranging from ~50° to 85°. To further improve wettability of these materials, they were subjected to $H_2O$ (v) plasma modification, an approach that has been successful in past studies to improve polymer biocompatibility. After plasma treatment, wettability increased, with water contact angles of ~20-35°, and the films exhibited a significant enhancement in oxygen content (40-150%), while remaining stable in aqueous solutions. Attachment and biofilm formation assays allowed for assessment of bacterial interactions at 1 and 5 days after exposure, respectively, with gram-negative *E. coli* and gram-positive *S. aureus*. Using microscopy techniques, we observed attachment and growth are substantially diminished for as-deposited and $H_2O$ (v) plasma treated films. Moreover, performance data (i.e., flux of coated ultrafiltration membranes) are presented. Surface analysis and performance testing results, combined with information about gas phase excited state species observed using optical emission spectroscopy, guide our development of additional antibacterial essential oil-based films for 2D and 3D constructs used in environmental and biomedical applications.

8:20am **BI+NS-WeM2 Transition Metal Nanoparticles and Quantum Dots with Tunable Electronic Properties by Bacterial Precipitation: Synthesis and Applications**, *K.E. Marusak, Y. Feng, E. Ngaboyamahina, Y. Cao, J.T. Glass, L. You*, ***Stefan Zauscher***, Duke University

We present a new method for the fabrication of semiconducting, transition metal nanoparticles (NPs) with tunable bandgap and useful photoelectric properties, through bacterial precipitation. *Escherichia coli* bacteria have been genetically engineered, by overexpression of a cysteine desulfhydrase gene, to precipitate transition metal NPs from solution, here more specifically, cadmium sulfide (CdS). Transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) revealed that the bacterially precipitated NPs are agglomerates of mostly quantum dots (QDs), with a diameter of 4-5 nm, in a carbon-rich matrix. We discovered that the precipitation conditions of the bacteria can be tuned to produce NPs with bandgaps that range from quantum-confined to bulk CdS. Furthermore, we determined their photoelectrochemical (PEC) properties and their energy band structure by electrochemical measurements. In addition, by taking advantage of the organic matrix, which is residual from the biosynthesis process, we fabricated a prototype photocharged capacitor electrode by incorporating the bacterially precipitated CdS with a reduced graphene oxide (RGO) sheet. Our results show that bacterially precipitated CdS NPs are potentially useful components for PEC devices with applications for energy conversion and storage.

References:

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8:40am **BI+NS-WeM3 Plasma Surface Modification of 2D and 3D Constructs: Creating and Evaluating New Materials for Biomedical Applications**, ***Ellen Fisher***, Colorado State University **INVITED**

Plasma processing represents a powerful approach to modification of 2D and 3D substrates with an array of chemistries appropriate for use in biomedical applications. It is an attractive methodology because of its versatility, low waste, and scalability. The three major plasma surface modification classifications are deposition (film formation, polymerization), etching (removal of material) and functional group implantation (covalent bonding of chemical functional groups), which collectively provide a large landscape for creating materials with specific properties tailored for particular applications. Combining a range of spectroscopic techniques, materials characterization tools, and basic biological interaction studies provides a platform for deeper insight into these underlying mechanisms than just one approach alone. Yet, this can also lead to a range of obstacles, especially when seeking to apply traditional diagnostic methodologies to new systems and materials. For example, data on the surface chemistry of 3D constructs coated with thin films having a range of film chemistries (via utilization of allylamine/allylalcohol mixed gas plasmas) combined with an understanding of the gas-phase chemistry in these systems and cell-surfaces interaction studies highlights key properties required to tune the surface chemistries that can promote or deter cell viability and proliferation. Thus, this presentation will highlight a few key examples, including inherent challenges, where such a unified, comprehensive approach has been fruitful for 2D and 3D materials intended for use as antimicrobial materials, in separations, and for tissue engineering applications.

9:20am **BI+NS-WeM5 The Ins and Outs of Functionalized Natural Materials for Applications in Drug Delivery and Separations**, ***Norma Alcantar****, R. Toomey, Z. Veisi,* University of South Florida*, A. Cardenas-Valencia, M. Cardenas,* SRI International*, R. Falahat,* Moffitt Cancer Center, *T. Peng, F. Guo*, University of South Florida **INVITED**

In the last decade, numerous natural materials have been investigated as platforms in functionalized surfaces. In our case, we have studied the structure and properties of two natural materials, chitosan from crustaceous shells and cactus mucilage from cactus plants. Those two natural materials have been used as building blocks in drug delivery systems, and as flocculants or adsorbent materials to remove contaminants from water. In the drug delivery systems, the natural material is used as surface membranes capable to respond to external stimuli. Our team has discovered that chitosan has a specific bond with the MUC1 enzyme found in epithelial-type cancers, which can enhance its specificity towards cancer cells when used in drug delivery systems. The results of our research have also shown that depending on the biophysical conditions surrounding the natural materials, their response to hydrophilic and hydrophobic interactions to separate organic and inorganic contaminants are controlled by their structure, which can then be finely tuned to enhance their performance. The use of natural materials for functional applications is an area of study that could lead to discoveries in microfluidic devices, health applications, cosmetics, coatings and paintings, and water purification systems.

11:00am **BI+NS-WeM10 Combinatorial Material Chemistry-Topography Screening: The ChemoTopo Chip**, ***Britta Koch*****, University of Nottingham, UK, *A. Vasilevich, N. Beijer, J. de Boer,* Maastricht University, The Netherlands, *M.R. Alexander*, The University of Nottingham, UK

The interaction of cells with their culture substrate is critical to their fate, having a profound impact on cell response and viability. However, complex cell-cell as well as cell-matrix interactions in native tissue make it challenging to emulate *in vivo* cell behavior in the lab. The design of man-made, biomimetic cell environments hold great potential for biomedical applications like tissue engineering, disease modeling and drug screening. Therefore, suitable biomaterials are sought that can interface with cells and provide adequate physical, chemical and biological characteristics to elicit the desired cell response in a well-defined *in vitro* environment.

In recent years, microarray technology in combination with high-throughput surface characterization methods has proven to be a valuable tool for the cost-efficient and rapid screening of large libraries of biomaterial candidates. However, until now screening has been performed either on planar samples, focusing on optimizing sample chemistry rather than topography [1] or on topography with no chemical variation [2]. Here we propose a novel platform that augments the chemical screening approach with deterministic control of the topography. This new platform called the ‘ChemoTopo Chip’ allows the systematic investigation of combinatorial effects of well-defined surface chemistry and topography and moves closer to recapitulating the range of 3D cues at play *in vivo* within an *in vitro* screen. The first results on the identification of hit combinations supporting mesenchymal stem cell growth are presented and future steps aiming at enhancing our global understanding of the context-dependent cell response are outlined. The ChemoTopo Chip platform contributes to the discovery of novel substrates with the potential to ultimately translate these into biomedical applications. Also, the gathering of data allows to develop surface structure-property relationships from which understanding can be generated to support rational design of the *in vitro* cell environment.

[1]. Y. Mei, K. Saha, S. R. Bogatyrev, J. Yang, A. L. Hook, Z. I. Kalcioglu, S.-W. Cho, M. Mitalipova, N. Pyzocha, F. Rojas, K. J. Van Vliet, M. C. Davies, M. R. Alexander, R. Langer, R. Jaenisch, D. G. Anderson. *Nature Materials* 9, 768-778 (2010).

[2]. H. V . Unadkat, M. Hulsman, K. Cornelissen, B. J. Papenburg, R. K. Truckenmüller, A. E. Carpenter, M. Wessling, G. F. Post, M. Netz, M. J. T. Reinders, D. Stamatialis, C. A. Bitterswijk, J. de Boer. *PNAS* 108, 16565-16570 (2011).

11:20am **BI+NS-WeM11 Combining Surface Analytical and Computational Techniques to Investigate Orientation Effects of Immobilized Proteins**, ***Elisa Harrison****, G. Interlandi, D.G. Castner*, University of Washington, Seattle

Controlling how proteins are immobilized (e.g. controlling their orientation and conformation) is essential for developing and optimizing the performance of *in vitro* binding protein devices, such as enzyme-linked immunosorbent assays. The objective of this work is to develop new methodologies to study proteins and complex mixtures of proteins immobilized onto surfaces.

The focus of this study was to control and characterize the orientation of protein G B1, an IgG antibody-binding domain of protein G, on well-defined surfaces as well as measure the effect of protein G B1 orientation on IgG antibody binding using a variety of surface analytical and computational techniques. The goal was to immobilize protein G B1 into well-ordered films with different orientations that control the accessibility of antibody binding sites.

The surface sensitivity of time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to distinguish between different proteins and their orientation by monitoring the changes in intensity of characteristic amino acid mass fragments. Amino acids with asymmetric distributions (Asn, Trp, Gly, Ala, and Thr) were used to calculate peak intensity ratios from ToF-SIMS data in the C- and N-terminus of protein G B1 to determine the orientation of five different cysteine mutants of protein G B1 covalently attached to a maleimide surface.

To study the effect of protein orientation on antibody binding, we formed multilayer protein films. Quartz crystal microbalance with dissipation monitoring (QCM-D) detected protein coverages of 69 - 130 ng/cm$^2$. QCM-D and X-ray photoelectron spectroscopy (XPS) analysis revealed that packing density along with orientation affected the antibody binding process. Spectra from ToF-SIMS using large Ar gas cluster ion sources distinguished between different proteins in multilayer protein systems.

Additionally, development of computational methods to study proteins on surfaces can complement surface analytical data. A Monte Carlo algorithm was developed to predict protein orientation on surfaces. Two distinct orientations of protein G B1 adsorbed onto a hydrophobic surface were found and characterized as two mutually exclusive sets of amino acids on the outermost β-sheets contacting the surface. This prediction was consistent with sum frequency generation (SFG) vibrational spectroscopy results. In fact, theoretical SFG spectra calculated from an equal combination of the two predicted orientations exhibited reasonable agreement with measured spectra of protein G B1 on polystyrene surfaces. This method has been expanded to predict protein G B1 orientations on more complex surfaces, such as self-assembled monolayers.

11:40am **BI+NS-WeM12 Characterizing the Tumor Microenvironment and Tumor Progression**, ***Blake Bluestein***, University of Washington, *F. Morrish, D. Hockenbery,* Fred Hutchinson Cancer Research Center, *L.J. Gamble*, University of Washington

Solid tumors are not simply masses of malignant cells but are a structurally complex system, composed of a myriad of cells. The interactions between malignant cells and non-transformed cells form the tumor microenvironment. The tumor microenvironment has been associated with regulating tumor cell

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* **BID Early Career Researchers Award**

growth, metastatic potential, and drug resistance. Here, a combination of techniques including imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS), H&E staining, and second harmonic generation (SHG) microscopy are used to analyze pancreatic biopsies from a mouse model with Myc-dependent inducible pancreatic β-cell neoplasia to relate changes in the composition and distribution of metabolic related molecules with tumor development. Myc, one of the most frequently deregulated oncogenes in human cancers, contributes to tumorigenesis through various mechanisms, including the deregulation of cell proliferation and metabolic alterations.

Pancreatic tissues were harvested and frozen in optimal cutting temperature (OCT) at 6 days post Myc induction and without any Myc induction (control). Cryosections (4 µm thickness) were serially cut, with one used for H&E staining and SHG microscopy, and one for ToF-SIMS analysis. ToF-SIMS data was acquired using an IONTOF TOF.SIMS 5. Regions identified by analysis and principal components analysis (PCA) were cross-referenced against immunohistochemical, H&E, and SHG images to differentiate the tumor areas from the surrounding tissue.

PCA analysis of ToF-SIMS image data separate tumor from surrounding tissue and reveal the differences in chemistries between the two regions. The Myc-induced islet tumors exhibit a signal of C14:0, a likely product of *de novo* fatty acid synthesis within the islet tumor. Image data shows higher signal regions within the interior of the tumor. These regions exhibit an increased, localized signal of CN$^-$, CNO$^-$, Fe$^+$, and characteristic histidine fragments, $C_5H_8N_3^+$ and $C_6H_5N_2O^+$. SHG images showed that there were no organized structures in these higher signal regions and immunohistochemistry showed no signs of angiogenic processes, confirming that these areas are blood pools resulting from vascular hemorrhaging. Further metabolic analyses showed that when compared to control islets, Myc-induced tumor islets exhibited increased intensities of amino acids and phosphatidylcholine lipids (30:0, 32:1, 32:2), which are known to be related to tumor growth. Tissue surrounding the Myc islet tumors exhibited lower intensities of serine, glycine, and arginine when compared to the tissue surrounding the control islets, which suggests tumor uptake or an increased catabolism induced by the adjacent tumor.

12:00pm **BI+NS-WeM13 Observing the Molecular Mechanisms of Insect Adhesion by Sum Frequency Generation Spectroscopy**, *J.E. Fowler,* Oregon State University, *S.N. Gorb*, Kiel University, Germany, *T. Weidner*, Aarhus University, Denmark, ***Joe Baio***, Oregon State University

Many insects can walk on a range of natural surfaces through an adhesion process that combines an expansive array of hairy contacts on their feet, known as setae, and an adhesive fluid, forming contact between the setae and a substrate. Previous studies of this adhesion system have focused almost exclusively on the mechanical and kinematic aspects of adhesion, while ignoring the molecular interactions at the fluid – substrate interface. However, recent experiments illustrate that substrate chemistry does influence the adhesive forces produced by this fluid. Additionally, mass spectrometry results demonstrate that this adhesive fluid is a complex mixture containing both hydrophobic (*i.e.* fatty acids and lipids) and hydrophilic (*i.e.* sugars, alcohols, and carbohydrates) compounds. We hypothesize that the molecular structure at the adhesive fluid-substrate interface is dynamic, with different molecules within the fluid selectively organizing at the interface as a function of substrate hydrophobicity. In the work presented here we probe the molecular interactions between the adhesive fluid taken from lady bugs (*Cocinella septempunctata*) and three model substrates, polyethylene oxide, polystyrene and $CaF_2$ with vibrational sum frequency generation (SFG) spectroscopy and scanning electron microscopy (SEM). The observed water contact angles for the polyethylene oxide, polystyrene and $CaF_2$ substrates were $66^o$, $92^o$ and $106^o$, respectively. High-resolution SEM images of individual seta-fluid footprints on the surfaces indicate localized "water in oil" emulsion de-wetting with no sign of distinct patterning. SFG spectra collected, from the three substrates, at the C-H (2800-3100 cm$^{-1}$) contain peaks at 2850 cm$^{-1}$ and 2870 cm$^{-1}$, characteristic of symmetric $CH_2$ and $CH_3$ stretches, respectively. The presence of these peaks suggests an ordered hydrocarbon monolayer at the interface. However, subtle changes in ordering of these molecular groups at the interface were observed across substrates by comparing the ratio of the intensities of observed vibrational modes related to the $CH_2$ and $CH_3$ modes. Across the three different substrates this ratio increased with surface hydrophobicity suggesting that the fluid-surface interactions adapt to different substrate chemistries.

## Electronic Materials and Photonics Division
## Room: 14 - Session EM-WeM

## Charge Transport in Disordered Materials

**Moderator:** Michelle Paquette, University of Missouri-Kansas City

8:00am **EM-WeM1 Electrons and Phonons in Amorphous Semiconductors**, ***David Drabold***, *K. Prasai*, Ohio University, *P. Biswas*, University of Southern MIssissippi **INVITED**

The coupling between lattice vibrations and electrons is one of the central concepts of condensed matter physics. The subject has been deeply studied for crystalline materials, but far less so for amorphous and glassy materials, which are among the most important for applications. In this talk, we explore the electron-lattice coupling using current tools of first-principles computer simulation. We choose three materials to illustrate the phenomena: amorphous silicon, amorphous selenium, and amorphous gallium nitride. In each case, we show that there is a strong correlation between the localization of electron states and the magnitude of thermally-induced fluctuations in energy eigenvalues obtained from density-functional theory (i.e. Kohn-Sham eigenvalues). We provide a heuristic theory to explain these observations. The case of amorphous GaN, a topologically disordered partly ionic insulator, is distinctive compared to the covalent amorphous systems. We close by showing how the optical gap of an amorphous semiconductor can be computationally engineered with the judicious use of Hellmann-Feynman forces (associated with a few defect states) using molecular dynamics simulations. These forces can be used to close or open an optical gap, and identify a structure with a prescribed gap. We use the approach with plane-wave density functional methods to identify the conducting state of a conducting bridge memory material: Ag-doped $GeSe_3$.

K. Prasai, P. Biswas and D. A. Drabold, *Electrons and Phonons in Amorphous Semiconductors*, Semicon. Sci. Tech. **31** 073002 (2016).

8:40am **EM-WeM3 Percolation Resistivity in Nanostructured Transparent Conductor Networks Consisting of Curvy Nanowires**, ***Junying Li***, *C. Ying, J. Hicks, A. Ural*, University of Florida

Transparent, conductive electrodes have many applications in electronic and photonic devices such as touch screens, solar cells, LEDs, and photodetectors. Metal nanowire networks are promising candidates for these applications as a replacement for indium tin oxide, which has problems such as high cost, scarcity, and brittleness. The conduction in metal nanowire networks is governed by percolation theory.

In most computational work, nanowires in these networks have been modeled as straight "sticks". However, in real experiments, individual nanowires are not perfectly straight, but exhibit some degree of curviness. In this work, we perform systematic Monte Carlo simulations to study the effect of nanowire curviness on the scaling of percolation resistivity in nanowire networks. We generate the curved nanowires using 3$^{rd}$-order Bézier curves. These curves are endowed with a curviness angle property that specifies how far away the two intermediate control points of the Bézier curve may lie, in the tangential sense, from a straight path connecting the two ends of the curve. The curviness angle is varied to obtain networks of differing values of curl ratio, which is defined as the ratio between the curved length of a nanowire and the straight distance between its two ends.

We find that, for random networks, the resistivity of the network increases with increasing nanowire curviness and the resistivity exhibits an inverse power law dependence on the curl ratio. We also find that the value of the extracted inverse power law critical exponent is not universal, but depends on other nanowire and device parameters. As a result, we also study the effect of nanowire density, nanowire length, device length, device width, and nanowire alignment angle on the scaling of network resistivity with nanowire curl ratio.

Curviness results in two competing effects on the percolation resistivity. First, curviness decreases the effective length of the nanowire between its two ends, which increases the resistivity. Second, it increases the effective width of the nanowire, which decreases the resistivity. For networks with aligned nanowires, we find that increasing the curviness decreases the resistivity, indicating that the second effect starts to dominate. By simulating networks with varying values of alignment angles, we study the crossover from the first to the second regime.

These results show how the degree of curviness of individual nanowires contributes to the macroscopic resistivity of the network. They also show that computational studies are an essential tool for providing insight into the percolation transport in transparent, conductive nanowire networks.

9:00am **EM-WeM4 Surface Chemical Control of Charge Transport and Infrared Plasmonic Response in Nanocrystal Thin Films**, ***Dmitriy Boyuk***, *W. Hu, M.A. Filler*, Georgia Institute of Technology

Infrared plasmonic nanocrystal thin films are promising materials for harvesting thermal radiation, but their use requires an ability to simultaneously control nanocrystal carrier density and interfacial charge transport. Here, we combine *in situ* infrared spectroscopy and nanoscale four-point probe measurements to show the intimate interplay between nanocrystal surface chemistry, the localized surface plasmon resonance (LSPR), and thin film resistivity. Indium tin oxide (ITO) nanocrystals synthesized via colloidal methods exhibit LSPRs tunable in the mid-infrared (from 0.2 to 0.6 eV) and serve as model infrared plasmonic materials with which to study these effects. Removal of surface hydroxyl groups, via reaction with metal alkyl species (e.g., trimethylaluminum), and formation of a monolayer of oxygen-metal surface bonds (e.g., Al-O) reduces the number of nanocrystal surface traps. The corresponding increase in carrier density is evidenced by a clear blue shift and increase in intensity of the LSPR. This monolayer surface treatment decreases nanocrystal film resistivity by two orders of magnitude (to 1 x $10^{-2}$ ohm-cm). We further demonstrate that conformal coatings (e.g., of $Al_2O_3$ or ZnO) permit control of nanocrystal thin film resistivity without modifying LSPR energy, a capability that allows us to independently engineer light absorption and device properties. We also find that these plasmonic nanocrystal films exhibit a photoconductivity in response to mid-infrared light illumination.

9:20am **EM-WeM5 Study of Cation Exchange and Transport in Crystalline Solids Through Density Functional Theory Calculations**, ***Daniel Dumett Torres***, University of Illinois at Urbana-Champaign

Ion transport is closely tied to chemical transformations of crystalline ionic solids such as impurity doping and ion exchange. In order to introduce heteroatoms and other impurities into a crystal it is necessary to displace ions, create vacancies, and fill vacancies many times to achieve a significant degree of transformation. Thus ionic mobility plays a deterministic role both as to how fast a transformation occurs and the achievable extent of doping/exchange in a given system. For example exchange of $Cd^{2+}$ for $Cu^+$ in CdSe nanocrystals occurs rapidly and full conversion is ultimately reached. However replacing $Cd^{2+}$ for $Hg^{2+}$ does not reach completion and proceeds more slowly. A full explanation for how these two processes differ must address the mobility difference between $Hg^{2+}$ and $Cu^+$ through the $Se^{2-}$ sublattice.

As a separate example: fast ion conduction relies on there being extensive ion transport in a solid. Such transport could be facilitated by cooperative effects, low ($<k_bT$) activation energy barriers against ion migration, or a combination of these and other factors. An understanding for how ionic mobilities differ and how they might be manipulated or enhanced will guide the design of materials such as nanoscale semiconductors for applications in optoelectronics, solid state battery electrolytes, and thermoelectrics. Specifically, control over superionic phase transitions can make new materials available for applications in solid state electrolytes by permitting new superionic conductors to be realized at working conditions as opposed to at elevated temperatures.

The approach is to employ density functional theory (DFT) electronic structure calculations for the elucidation of ion conduction trends in $Li_xCu_{2-x}Se$. The $Li_xCu_{2-x}Se$ alloys vary in their fraction of $Li^+$ or $Cu^+$ cations both of which are mobile and thus apt for a study into tuning ion mobility. Total energies from DFT calculations for a large set of $Li_xCu_{2-x}Se$ structures permit the identification of factors that promote or inhibit ion mobility. By varying both the cation locations and cell parameters the energetic penalties associated with pushing cations from their relaxed positions into interstitial sites can be obtained. Coupled with a exploration of the $Li_xCu_{2-x}Se$ compositional range, the DFT energies reveal the best alloys for cation transport that have the lowest energetic penalties and smallest activation barriers. Complementary calculations in which the simulation cell volume is increased or decreased study the effects of tensile and compressive strain respectively; the calculated energies inform how strain and pressure can be used to control ion conduction.

9:40am **EM-WeM6 Probing Charge Transport in Amorphous Hydrogenated Boron Carbide**, ***Gyanendra Bhattarai***, *S. Dhungana, R. Thapa, T.D. Nguyen, A.N. Caruso, M.M. Paquette*, University of Missouri-Kansas City

Amorphous hydrogenated boron carbide is a complex disordered semi-insulating material being studied for neutron detection applications owing to its high thermal neutron absorption cross-section and high resistivity. Optimizing its charge transport properties, including charge carrier mobility, lifetime, and mobility-lifetime product, will be essential to successful detector implementation. Tuning these properties requires a clear understanding of the disorder in this solid, as well as charge injection and hopping via localized states, and how these phenomena lead to difficulties in experimental design as well as analysis of charge transport measurements. This contribution will present an overview of the challenges and nontrivialities in establishing electrical contacts and determining charge transport properties introduced by the disorder in the material, and our approaches to measurement and analysis.

11:00am **EM-WeM10 On the Abnormality in Mobility of ZnO Thin Film Transistors Based on Sol-Gel Deposited Channel Layers**, ***Vahid Mirkhani***, *K. Yapabandara, S. Wang, M.P. Khanal, S. Uprety*, Auburn University, *M.H. Sk*, Qatar University, Qatar, *A. Ahyi, M.C. Hamilton, M. Park*, Auburn University

Extensive research has been conducted on zinc oxide (ZnO) thin film transistors (TFTs) for the last couple of decades. Solution processes such as sol-gel are popular fabrication methods among researchers due to their simplicity and economical aspects. We have observed an abnormality in transconductance and mobility curve of the TFT with a channel layer prepared through sol gel spin coating process. Transconductance and mobility curves, determined from transfer characteristics, exhibit two peaks, instead of an expected single peak. We have rationalized the phenomenon by pondering the ZnO-ZnO interfaces. During the ZnO thin film deposition process, the spin coating and calcination steps are repeated multiple times in order to achieve a desirable layer thickness. When a layer is deposited, prior to the second spin coating step, the vacancies on the layer surface (comprised of grain boundaries of different grains) act as active sites, adsorbing molecules from the ambient. The adsorption of gasses such as oxygen and water molecules on ZnO structure surfaces has been studied for several decades; although the detailed kinetics and chemical reactions are debatable. Moisture and oxygen may be chemisorbed on the surface by receiving an electron and form a trapped negative ion on the surface, forming a depletion region at the surface of the layer. Oxygen may capture an electron and react with oxygen vacancies ($V_O$ and $V_O^+$), in order to form chemisorbed ions such as $O^-$, $O^{2-}$ or $O_2^-$, whereas $H_2O$ may form $OH^-$ on the surface. Potential barriers created at the interlayer interfaces are wider and higher than the regular barriers created at the grain boundaries in the bulk. The interlayer interface depletion layers formed by negative ions will not be affected by the annealing process due to their stability at room temperature. Thus, the initial ZnO-ambient interface (prior to the next layer-deposition process) evolves into the ZnO-ZnO interlayer interface. The significance of the depletion layers at the ZnO-ZnO interfaces becomes evident when the carriers are not able to drift across these interfaces at gate voltages smaller than a critical voltage ($V_C$). As the gate voltage increases, the width of the depletion regions decrease and carriers are able to tunnel through the barriers with ease and utilize all the deposited layers as a single channel and hence, an increase in the transconductance and mobility and later, a second peak. It is proposed that the first peak is related to the formation of the channel in the top layer and the second peak is assigned to all the deposited layers acting as a single-layer-channel.

11:20am **EM-WeM11 Electrical Characterization and Localized Density of States Extraction of Thin-Film Transistors Based on Sol-Gel Derived ZnO Channel Layers with Different Annealing Temperatures**, ***Shiqiang Wang***, *R. Cheng, M.C. Hamilton, V. Mirkhani, K. Yapabandara, S. Uprety, A. Ahyi, M. Park,* Auburn University, *M.H. Sk*, Qatar University, Qatar

We report on the fabrication and electrical characterization of bottom gate thin-film transistors (TFTs) based on sol-gel derived ZnO channel layer. The effect of annealing of ZnO active channel layers on electrical characteristics of the ZnO TFTs was systematically investigated. Photoluminescence (PL) spectra indicate that the crystal quality of the ZnO improves with increasing annealing temperature. Both the device turn-on voltage ($V_{on}$) and threshold voltage ($V_T$) shift to a positive voltage with increasing annealing temperature. As annealing temperature is increased, both the subthreshold slope (*SS*) and the interfacial defect density ($D_{it}$) decrease. The field effect mobility ($\mu_{FET}$) increases with annealing temperature, peaking at 800 °C and decreases upon further temperature increase. Besides that, the temperature dependent field effect measurement (from 296 K to 330 K) was used to gain an insight on the annealing temperature effect on sol-gel derived ZnO TFTs electrical characteristics. The conduction processes in these TFTs are thermally activated and the drain current, especially in subthreshold regime, obeys Arrhenius equation. Thermal activation energy and a corresponding prefactor parameter were extracted from temperature dependent field effect measurement. The Meyer-Neldel (MN) rule widely observed in the intrinsic material property study is also obeyed by the relation between thermal activation energy and the prefactor parameter. By combing the MN rule and applying the self-consistent procedure, the localized sub-gap density of states ( DOSs) of different temperature annealed sol-gel derived ZnO TFTs were successfully extracted. The DOSs for subthreshold regime decrease from $10^{19}$ $eV^{-1}cm^{-3}$ level to $10^{17}$ $eV^{-1}cm^{-3}$ level with increasing annealing temperature from 600 °C to 800 °C and no substantial change was observed with further temperature increase to 900 °C. The results show that DOSs decrease with annealing temperature increase in general, but annealing at a very high temperature may not be beneficial to reducing DOSs. It was found that the TFTs with ZnO layers annealed at 800 °C for one hour shows the best electrical performance with the highest field effect mobility and lowest localized DOSs.

11:40am **EM-WeM12 Real-space Characterizations of Photo-generated Carriers in P3HT-based Nanostructures using Kelvin Probe Force Microscopy**, ***Eunah Kim***, *S. Kwon, D.H. Kim*, Ewha Womans University, Republic of Korea, *H.-H. Park,* Korea Advanced Nano Fab Center, Republic of Korea, *J. Kim,* Incheon National University, Republic of Korea, *D.-W. Kim*, Ewha Womans University, Republic of Korea

Organic-inorganic hybrid nanostructures have been proposed to improve the performance of organic photovoltaic devices. In this work, we investigated creation and transport behaviors of photo-generated carriers in P3HT-based hybrid nanostructures, such as P3HT-coated Si-nanopillar (NP) arrays and P3HT layers with embedded upconversion nanorods (UCNs). Optical resonance strongly concentrated incident light in the Si NPs, significantly increasing the number of photo-carriers near the NPs. The UCNs converted near-infrared (NIR) light to visible light . We studied spatial distribution of the surface photovoltage (SPV) in the P3HT/Si-NP and P3HT/UCN samples using Kevin probe force microscopy. The magnitude and sign of SPV are determined by the number of the photo-carriers and band profiles near the sample surface [1-3]. Large SPV values appeared in the P3HT layers near the Si NPs under illumination of visible light and near the UCNs under illumination of NIR light in the P3HT/Si-NP and P3HT/UCN samples, respectively [3,4]. This suggested that the concentrated light in the NPs and photon upconversion in the UCNs increased the local density of photo-carriers. Our work shows that the scanning probe microscopy technique can visualize the creation and transport behaviors of photo-generated carriers in nanostructures.

1. E. Kim et al., *Curr. Appl. Phys.***16**, 141 (2016).
2. M. Gwon et al., *Sci. Rep.***5**, 16727 (2015).
3. E. Kim et al., *Sci. Rep.***6**, 29472 (2016).
4. Y. Jang, E. Kim et al., *J. Phys. Chem. Lett*. **8**, 364 (2017).

12:00pm **EM-WeM13 Electrically Detected Magnetic Resonance Study of the Relationship Between Silicon Nitride Stoichiometries and Defect Structure and Energy Levels**, ***Ryan Waskiewicz***, Pennsylvania State University, *M.J. Mutch*, Micron Technology, *P.M. Lenahan*, Pennsylvania State University, *S.W. King*, Intel Corporation

Leakage currents in dielectric thin films utilized in present day integrated circuitry are important reliability concerns. Among the most important dielectric materials are amorphous hydrogenated silicon nitrides (a-SiN:H). These relatively high dielectric constant materials are utilized in many applications such as a passivating layer, an etch stop layer, a diffusion barrier to water, and a gate dielectric. Electron paramagnetic resonance (EPR) studies of a-SiN:H films have identified the K center (a silicon dangling bond back-bonded to three nitrogen atoms) as the single dominating paramagnetic defect in stoichiometric films. Previous studies of spin dependent trap assisted tunneling (SDTAT) detected via electrically detected magnetic resonance (EDMR) provide us with energy levels for these K center defects.[1] However, the effects of varying N/Si stoichiometry on defect levels and defect chemistry have not been studied with EDMR. We have initiated such an EDMR study of SDTAT in a-SiN:H dielectric samples of several stoichiometries.

In our SDTAT/EDMR measurements, a slowly varying magnetic field and an oscillating rf or microwave frequency magnetic field are applied to the thin film samples. As in conventional EPR, energy is absorbed by paramagnetic sites when the resonance condition is met. In the simplest cases, this condition may be expressed by hv=guB, where *h* is Planck's constant, g is an orientation dependent parameter often close to 2, u is the Bohr magneton, and B is the magnetic field. In EDMR, the EPR is detected through a change in current, in our case due to SDTAT.

The devices in our study include 3 nm a-SiN:H stoichiometric samples, and 25 nm a-SiN:H samples with three N/Si ratios of 1, 1.35, and 1.5. The overall device structures under observation consist of Ti/a-SiN:H/p-Si capacitors. A comparison of EDMR measurements taken at high field and frequency (X-band frequency ~ 9.75GHz, 3500G) and low field and frequency (frequency ~ 85-350MHz, 30-125G) provide us with information about defect structure. These comparisons allow us to extract information about the g matrix as well as hyperfine interactions. (The g and hyperfine details provide information about defect structure.) A comparison of EDMR measurements under various biasing conditions allow us to approximately determine the energy levels of the defects involved. This energy level and defect structure information should lead to a better understanding of transport in these technologically important materials.

[1] M.J. Mutch, P.M. Lenahan, and S.W. King, *Appl. Phys. Lett.* **109**(6), 062403 (2016).

## Exhibitor Technology Spotlight Workshops
## Room: West Hall - Session EW-WeM

### Exhibitor Technology Spotlight Session
**Moderator:** Chris Moffitt, Kratos Analytical, Inc.

10:20am **EW-WeM8 State-of-the-art Pump Technologies for Clean High and Ultra-high Vacuum**, *M. Audi*, Agilent Technologies, Italy, ***Jim Ramsden***, Agilent Technologies

A close-up look at recent developments in pump technologies that deliver clean high and ultra-high vacuum, with a focus on the benefits for research applications in those regions. Come see the new quiet, hermetic IDP dry scroll pumps which deliver excellent performance and require only simple, infrequent maintenance. We'll also be looking at the most recent TwisTorr FS turbomolecular pumps with robust floating suspension and exceptional light gas pumping capability, which permit the use of smaller primary pumps than other turbos of the same size. And we'll have look at the new VacIon Plus 200, the first ion pump with maximum pumping speed at low pressure, as well as a preview of some new developments for UHV.

## Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
## Room: 24 - Session HC+NS+SS-WeM

### Nanoscale Surface Structures in Heterogeneously-Catalyzed Reactions
**Moderator:** Erin Iski, University of Tulsa

8:00am **HC+NS+SS-WeM1 The Role of Nanoparticle Edges in Water Dissociation and Oxidation/reduction Reactions in Layered Cobalt Oxides Supported on Au(111) and Pt(111)**, ***Jakob Fester***, *J.V. Lauritsen,* Aarhus University, Denmark, *M. Garcia-Melchor*, Trinity College Dublin, *A.S. Walton*, University of Manchester, UK, *M. Bajdich*, Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, *A. Vojvodic,* University of Pennsylvania, *Z. Sun, J. Rodríguez-Fernández*, Aarhus University, Denmark

Nanostructured cobalt oxides show great promise as earth-abundant and cheap heterogeneous catalysts, in particular for the oxygen evolution reaction (OER) in electrochemical water splitting and low temperature CO oxidation. However, despite the strong potential in this system as catalysts, we still lack basic knowledge on the active sites and the exact reaction pathways as well as an understanding of the underlying principles behind observed synergistic effects with gold.

To study the possible structure and location of catalytically active sites under controlled conditions, we created a model system consisting of 2-dimensional layered cobalt oxide ($CoO_x$) nanoislands supported on Au(111) [1] and Pt(111) [2] substrates. This system offers the possibility to reveal the structures in atomic detail by Scanning Tunneling Microscopy (STM) combined with high-resolution X-ray Photoelectron spectroscopy (XPS).

By recording in-situ STM movies during exposure of Co-O bilayer nanoislands to $H_2O$ we showed that $H_2O$ dissociates on edge sites of the nanoclusters followed by migration of H to the basal plane which serves as a reservoir [3] . In combination with Density Functional Theory (DFT) calculations, a preferable dissociation pathway was revealed, also highlighting an assisting role of a second water molecule in the dissociation process.

The determining role of edge sites in the nanoparticle reactivity was further emphasized by STM and XPS studies capturing several stages in both of the gradual oxidation- and reduction processes leading to transitions between layered Co-O bilayer and O-Co-O trilayer morhphologies. In particular, atom-resolved STM images showed changes in edge structure and high densities of defect lines prior to the intercalation of oxygen. The onset of the O-Co-O trilayer formation is located at the island edges on both Au(111) and Pt(111), however several substrate effects were observed on the process rate, mechanism and reversibility. In general, the microscopic picture revealed in these studies suggests that special sites at $CoO_x$ nanoparticle edges may be important for the integral description of $CoO_x$ as a catalyst.

1. Fester, J., et al., Gold-supported two-dimensional cobalt oxyhydroxide (CoOOH) and multilayer cobalt oxide islands. Physical Chemistry Chemical Physics, 2017. **19**(3): p. 2425-2433

2. Fester, J., et al., Comparative analysis of cobalt oxide nanoisland stability and edge structures on three related noble metal surfaces: Au (111), Pt (111) and Ag (111). Topics in Catalysis, 2016: p. 1-10

3. Fester, J., et al., Edge reactivity and water-assisted dissociation on cobalt oxide nanoislands. Nature Communications, 2017. **8**

8:20am **HC+NS+SS-WeM2 Analysis of Bulk and Surface Properties of Catalytically-Active Nickel Carbide/Nitride Nanostructures using X-ray Techniques**, ***Samuel Gage***, *K. Fong, C. Ngo, S. Shulda,* Colorado School of Mines, *C. Tassone, D. Nordlund*, SLAC National Accelerator Laboratory, *R. Richards, S. Pylypenko*, Colorado School of Mines

Transition metal carbides and nitrides are an ever-growing topic in the scientific community. These materials can be synthesized with varying composition and morphology to exhibit properties similar to platinum-group metal catalysts, which are relevant to industrial heterogeneous catalysis and energy development. Studies, which report promising catalytic performances of nickel carbide and nitride catalysts, have continued to increase in recent years. Wet-chemical approaches involving a top-down thermal decomposition of nickel salt precursors in the presence of product-directing solvents are particularly interesting. The degree of nitrogen present in the nickel salt precursor, as well as the choice of molecular ligand-based solvents, can influence the material properties of the nickel carbide/nitride ($Ni_3C/Ni_3N$) products.

A series of nitrogen-rich and nitrogen-poor nickel salt precursors were thermally degraded in the presence of oleylamine. X-ray diffraction confirms the bulk hexagonal crystal structure belonging to $Ni_3C/Ni_3N$. However, a combination of bulk and surface X-ray characterization techniques, including the X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS), small angle- and wide angle X-ray scattering (SAXS and WAXS) indicate that the material properties of the $Ni_3C/Ni_3N$ nanostructures do vary depending on the precursor. Computationally guided experiments reveal that the unique bulk and surface properties of these nanostructures influence their catalytic activity, giving $Ni_3C/Ni_3N$ nanostructures the potential to be earth-abundant substitutes for precious metal catalysts.

9:00am **HC+NS+SS-WeM4 Grain-Boundary-Supported Active Sites for Electrochemical Catalysis**, ***Xiaofeng Feng***, University of Central Florida

Identification of active sites on a catalyst surface is the key to a rational design of heterogeneous catalysts. For nanoparticle catalysts, most efforts to tailor their surfaces have focused on controlling particle size, shape, and composition. The atomic surface sites underlying these structural features are mainly facets, steps, edges, and corner sites. These efforts have led to important progresses in heterogeneous catalysis, but it is unclear if the accessible structure space is sufficient for finding optimal catalysts. One alternative is to use bulk defects such as grain boundaries (GBs) to stabilize catalytically active surfaces. Here we show that the GBs in metal nanoparticles create new active sites for electrochemical catalysis. Through a careful design of metal nanoparticle catalysts with different GB densities, extensive TEM characterization, and electrochemical measurements, we discovered that the catalytic activity for $CO_2$ reduction on Au and CO reduction on Cu is linearly correlated with the GB density in the catalysts [1, 2]. The quantitative GB-activity relationship implicates GB surface terminations as new active sites and lead to highly active and stable electrocatalysts for a two-step conversion of $CO_2$ to liquid fuels such as ethanol and acetate. In addition, we found that the GBs in Au enhance its activity for oxygen reduction reaction, suggesting that GB engineering may be a general strategy to improve heterogeneous catalysis for renewable energy conversion.

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9:20am **HC+NS+SS-WeM5 Molecule-Surface Interaction on $TiO_2$ and $MoS_2$**, ***Zhenrong Zhang***, Baylor University **INVITED**

Interaction of molecules with surfaces of catalysts is critical for understanding catalytic reaction mechanisms. We have studied the interaction of various probe molecules with $TiO_2$ and $MoS_2$ using scanning tunneling microscopy (STM) and tip-enhanced Raman scattering (TERS). Two-dimensional material, $MoS_2$, has attracted tremendous attention due to promising applications in electronics, photonics, and catalysis. Here we compared the difference in the interaction of sub-monolayer copper phythalocyanine (CuPc) molecules with $MoS_2$ and Au. The relative Raman peak ratio and Raman peak position shift from s patial TERS mapping show the difference in the adsorbates-adsorbates interaction and the adsorbates-substrates interaction on Au and $MoS_2$ substrates. We have investigated the limits of Raman signal enhancement on $MoS_2$. Employing carboxylic acid, acetone, and formaldehyde as probe molecules, we studied how reactive sites affect the chemical activity of $TiO_2$(110). This unique methodology enables us to achieve the atomic-level understanding of the key elemental reaction steps — adsorption, dissociation, diffusion, and coupling reaction — taking place in heterogeneous catalytic reactions.

11:00am **HC+NS+SS-WeM10 Enantioselectivity: The Quintessential Structure Sensitive Surface Chemistry**, ***Andrew Gellman***, *P. Kondratyuk, D. Rienicker, M.A. Payne*, Carnegie Mellon University **INVITED**

Enantioselective heterogeneous catalysis and surface chemistry are quintessential forms of structure sensitive surface processes. Selectivity is driven purely by the diastereomeric relationship between the structural handedness of a chiral reagent or transition state and the structural handedness of a chiral surface. Enantioselectivity can be observed on naturally chiral metal surfaces with structures that are described as having flat low Miller index terraces separated by kinked step edges, therefore lacking mirror symmetry. This work has mapped the enantiospecific decomposition kinetics of tartaric acid (TA) and aspartic acid (Asp) on ~500 different single crystal planes exposed by the surfaces of Cu(111) and Cu(100) Surface Structure Spread Single Crystal ($S^4C$). $S^4Cs$ are single crystals polished into a spherical shape that exposes continuous distributions of surface orientations vicinal to primary orientation. During isothermal decomposition of TA and Asp , XPS has been used to map the temporal evolution of coverage at points across the Cu(111) and Cu(100) $S^4Cs$. The D- and L-TA (D- and L-Asp) coverage maps across the $S^4Cs$ following heating at 450 K to decompose ~70% of the initially adsorbed molecule reveal the symmetry of the substrate surface and the enantiospecific decomposition kinetics on the chiral surfaces with R- and S- orientations. The fourfold symmetry of the Cu(100) substrate is apparent, and the enantiospecificity of the decomposition kinetics is revealed by the spiral nature of the two maps and their opposite sense of handedness for D- and L-TA. These data can be analyzed to yield the enantiospecific rate constants for TA decomposition as functions of surface orientation.

11:40am **HC+NS+SS-WeM12 Understanding the Growth and Chemical Activity of Pt-Re Clusters on HOPG and Titania Surfaces**, ***Donna Chen***, *T.D. Maddumapatabandi, A.J. Brandt, G. Seuser*, University of South Carolina

The growth and chemical activity of bimetallic Pt-Re clusters supported on highly-oriented pyrolytic graphite (HOPG) and $TiO_2$(110) surfaces are studied as model systems for understanding Pt-Re catalysts in the water gas shift (WGS) and methanol oxidation reactions. STM experiments demonstrate that both Pt and Re atoms are mobile on unmodified HOPG surfaces and form large clusters that preferentially located at step edges. However, $Ar^+$ sputtering creates defect sites that serve as nucleation sites and result in smaller clusters with uniform size distributions. At high metal coverages, exclusively bimetallic clusters are formed from both the deposition of Pt on Re or Re on Pt. The cluster surfaces are Pt-rich even for the Re on Pt clusters due to the lower surface free energy of Pt compared to Re and the high mobility of atoms within clusters. Similarly, Pt-rich Pt-Re clusters have also been grown on titania supports. The activities of the Pt-Re bimetallic clusters are investigated in a microreactor coupled to an ultrahigh vacuum chamber so that the surfaces can be characterized by X-ray photoelectron spectroscopy (XPS) before and after reaction. In the WGS reaction, Re remains metallic, and Pt on Re surfaces exhibit higher activity than pure Pt. In methanol oxidation, oxygen-diffusion of Re to the surface occurs under reaction conditions, and the formation of volatile $Re_2O_7$ results in Re sublimation from the surface. Furthermore, the titania support appears to stabilize $Re_2O_7$ against sublimation, whereas Re oxidation is enhanced by the presence of Pt in the bimetallic clusters.

12:00pm **HC+NS+SS-WeM13 *Single Atom Alloys* for Efficient and Cost-effective Catalysis**, ***E. Charles Sykes***, Tufts University

Catalytic hydrogenations are critical steps in many industries including agricultural chemicals, foods and pharmaceuticals. In the petroleum refining, for instance, catalytic hydrogenations are performed to produce light and hydrogen rich products like gasoline. Typical heterogeneous hydrogenation catalysts involve nanoparticles composed of expensive noble metals or alloys based on platinum, palladium, rhodium, and ruthenium. We demonstrated for the first time how single palladium atoms can convert the otherwise catalytically inert surface of an inexpensive metal into an ultraselective catalyst. High-resolution imaging allowed us to characterize the active sites in single atom alloy surfaces, and temperature programmed reaction spectroscopy to probe the chemistry. The mechanism involves facile dissociation of hydrogen at individual palladium atoms followed by spillover onto the copper surface, where ultraselective catalysis occurs by virtue of weak binding. The reaction selectivity is in fact much higher than that measured on palladium alone, illustrating the system's unique synergy.

Our *single atom alloy* approach may in fact prove to be a general strategy for designing novel bi-functional heterogeneous catalysts in which a catalytically active element is atomically dispersed in a more inert matrix. Very recently we demonstrated that this strategy works in the design of real catalysts. Palladium/copper nanoparticles containing <2% palladium exhibited highly selective hydrogenation of phenylacetylene under realistic reaction conditions and platinum/copper nanoparticles perform the industrially important butadiene hydrogenation at lower temperature using just 1% platinum. Moreover, some of the best industrial alloy catalysts to date may already be operating via this mechanism, but there is currently no method to directly probe the atomic geometry of a working catalyst. Our scientific approach allows one to parse out the minimal reactive ensembles in an alloy catalyst and provide design rules for selective catalytic nanoparticle. *From another practical application standpoint, the small amounts of precious metal required to produce single atom alloys generates a very attractive alternative to traditional bimetallic catalysts.*

## 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-

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* **Falicov Student Award Finalist**

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 λ = 213nm 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 $\lambda$ = 213nm 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 $\gamma$-PNA. The results indicate that the adsorbed molecules act as a spin filter.

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## MEMS and NEMS Group
## Room: 16 - Session MN+2D-WeM

## 2D NEMS
**Moderators:** Zenghui Wang, Case Western Reserve University, Zhu Diao, Halmstad University/Stockholm University

8:00am **MN+2D-WeM1 Micro-patterned Graphene Temperature Sensors on Different Substrates**, *B. Davaji,* Marquette University, Cornell University*, H.D. Cho,* Dongguk University*, **Jong-Kwon Lee**,* National Nanofab Center in Korea*, T.W. Kang,* Dongguk University*, C.H. Lee,* Marquette University

Since the performance of electronic devices suffers from elevated temperatures as a result of self-heating, outstanding thermal properties of graphene are considered to be suitable for both instrumentation and integrated microelectronic applications [1]. Also, recently developed techniques for fabricating complex graphene structures in micro/nano scale [2, 3] make graphene a great candidate for temperature sensor applications due to its excellent electrical properties, outstanding mechanical strength, and high thermal conductivity.

In this study, micro-fabricated single-layer graphenes on a SiO2/Si, a SiN membrane, a suspended architecture, and a spatially nano-modulated Si substrate are presented for their use as temperature sensors. These graphene temperature sensors act as resistance temperature detectors, showing a quadratic dependence of resistance on the temperature. The observed resistance change of the graphene temperature sensors are explained by the temperature dependent electron mobility relationship (~ $T^4$) and electron-phonon scattering. The transient response analysis of the graphene temperature sensors on different substrates shows that the graphene sensor on the SiN membrane exhibits the highest sensitivity due to low thermal mass, whereas the sensor on SiO2/Si reveals the lowest one. In addition, the graphene on the SiN membrane reveals the fastest response, as well as better mechanical stability in comparison with the suspended graphene sensor. Therefore, we can expect that the graphene temperature sensors with an extremely low thermal mass will be used in various applications requiring high sensitive and fast operation.

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8:20am **MN+2D-WeM2 Characterizing the Resonant Behavior and Quality Factors of 3C-SiC Diaphragms Using Frequency Analysis and the Ring-Down Technique**, ***Yongkun Sui***, *H. Chong, K. Shara, C.A. Zorman*, Case Western Reserve University

Silicon carbide (SiC) has become a mainstream material for microelectromechanical systems (MEMS) due to its unique combination of outstanding electrical, mechanical and chemical properties, making it the preferred choice for applications in harsh environments where Si is not well suited. SiC is an attractive material for MEMS that utilize mechanical transduction due to its high Young's modulus, mechanical strength and chemical inertness. The cubic polytype of SiC (3C-SiC) is particularly attractive for resonant sensing applications because SiC diaphragms can readily be fabricated from thin films by Si bulk micromachining.

This abstract reports the findings of a study to characterize the resonant behavior of MEMS-based single crystalline 3C-SiC diaphragms. The 1 x 1 mm2 diaphragms consisted of 3C-SiC films that were heteroepitaxially grown on Si by APCVD and created by conventional bulk micromachining. The diaphragms were excited into resonance under vacuum using a piezoelectric PZT crystal and their vibratory behavior was assessed using a custom-built optical interferometer.

Over 20 resonant peaks were observed from a 250 nm-thick diaphragm for frequencies up to ~2 MHz. Quality factors were initially determined by analyzing the full-width-at-half-maximum of particular resonant peaks from the frequency spectrum. Although the fundamental mode exhibited a quality factor of ~3000, at least 3 other modes had high Q's of >20,000, with the highest being over 119,000. For those high quality factor resonance modes, the vibration energy took ~1 s to fully dissipate. As such, the frequency response had to be measured in a relatively slow manner otherwise the residual energy would propagate, resulting in a broadened peak. The ring-down test, which specifically characterizes the vibration energy dissipation rate, was used to measure the high quality factors. The highest Q at (2,3) mode was found to be 195,981 using ring-down test compared to 119,200 from the FWHM method. The resonance modes of the SiC diaphragm showed a non-linear Duffing behavior when the drive voltage exceeded 200 mV. The resonance peaks exhibited jump discontinuities and one of the half-power points ceased to be experimentally visible. In the nonlinear regime, quality factors measured by ring-down test differ only 1% from those in the linear region measured by both the FWHM and ring-down techniques.

8:40am **MN+2D-WeM3 Ion Radiation Effects in Silicon Carbide (SiC) Crystal Probed by Multimode Diaphragm Resonators**, ***Hailong Chen***, *V. Pashaei,* Case Western Reserve University*, W. Liao, C.N. Arutt,* Vanderbilt University*, H. Jia,* Case Western Reserve University*, M.W. McCurdy,* Vanderbilt University*, C.A. Zorman,* Case Western Reserve University*, R.A. Reed, R.D. Schrimpf, M.L. Alles,* Vanderbilt University*, P.X.-L. Feng,* Case Western Reserve University

Radiations effects from energetic particles (ions) and electromagnetic waves (photons) on electronics (*e.g.,* MOSFETs and ICs) have been widely investigated for applications in radiative harsh environments including space and nuclear reactors [1]. Radiation effects in mechanical domain, however, remain largely unexplored due to challenges in capturing and detection [2]. Meanwhile, most of preliminary studies on radiation effects in mechanical domain have been limited to Si structures and devices [3-4], while those on more intriguing radiation-durable materials such as SiC have not been investigated yet.

Here we report on experimental investigation and analysis of energetic ion radiation effects on silicon carbide (SiC) crystal, by exploiting a novel scheme of 4 vertically stacked resonant micromechanical SiC diaphragms. The SiC diaphragms are fabricated using a standard photolithographic and wet etching process to form resulting diaphragms (1 mm × 1 mm × 2.1 µm). An S-series Pelletron system is employed to irradiation oxygen ions into the SiC diaphragms (14.3MeV, 8h radiation, corresponding to a total fluence of $5.6 \times 10^{13}$/cm$^2$). Before and after radiation, multimode resonances are characterized in vacuum by using an ultrasensitive optical interferometry system. We have observed as large as ~9% frequency shifts (the largest value to date) in the multimode resonances of the 3rd diaphragm (counting from top in the stack) where most ions are expected to stop, as well as obvious quality (*Q*) factor degradation, which result from ionizing and displacement radiation damage. The 1st and 2nd diaphragms, which ions have mostly penetrated, exhibit moderate multimode frequency downshift of ~2% owing to displacement damage, while the 4th diaphragm shows the least frequency shift ~0.1%. The diaphragm stack exhibits outstanding capability for probing radiation damages in MEMS, not only able to capture the radiation events obviously but also help analyze different amount and types of damages induced in each stacking layer. Combining the data with a mixed elasticity model (that takes into account both flexural rigidity and pre-tension effects), we find: (i) the diaphragms operate in the *transition* regime (between '*plate*' and '*membrane*' but closer to the latter). (ii) after radiation behavior moves further towards the '*plate*' regime, suggesting reduction in *built-in tension* and possible reduction in Young's modulus as well.

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9:00am **MN+2D-WeM4 High-Aspect Ratio, Multi-Electrode, Carbon Nanotube Array**, ***Berg Dodson***, *G. Chen, R.R. Vanfleet, R.F. Davis*, Brigham Young University

We demonstrate a carbon nanotube based, high aspect ratio (~1 mm tall and 20 um diameter posts) multi-electrode array with individually addressable electrodes. The mechanical robustness and electrical conductivity of the carbon nanotubes make them a good candidate for the multi-electrode array. The electrode is made out of CNT posts which were grown on a patterned conductive substrate and kept vertically aligned with supporting hedges. The supporting hedges were subsequently removed to leave an isolated CNT post array. The fabrication method makes the structure compatible with a variety of surface coatings, including carbon, metals, and ceramics. Good electrical connection is made to individual elements of the array despite the insulating alumina barrier that is used between the substrate and CNT forests.

11:00am **MN+2D-WeM10 Interferometric Motion Detection in Atomic Layer 2D Nanoelectromechanical Systems (NEMS)**, ***Zenghui Wang***, University of Electronic Science and Technology of China, China, *P.X.-L. Feng*, Case Western Reserve University

Atomic layer crystals have emerged as a new class of two-dimensional (2D) materials, exhibiting great promises for both fundamental research and technological applications. Their outstanding mechanical properties make these materials ideal for constructing novel 2D nanoelectromechanical systems (NEMS), providing opportunities for coupling their material properties across multiple information-transduction domains, at scales down to individual atomic layers. One particularly interesting prototype of 2D NEMS is 2D nanomechanical resonators. While various electrical, mechanical, and optical motional signal transduction schemes have been employed for 2D NEMS resonators, laser optical interferometry [1][2] clearly stands out as one of the most important and widely used techniques. To date, it is the only technique capable to measure the completely undriven thermomechanical motions in these 2D nanostructures.

Toward pushing the ultimate limits, it is highly desirable to quantitatively understand the detection efficiency and its dependence on the device parameters and interferometric conditions. Here, we present a systematic study [3] of the intrinsic motion responsivity in 2D NEMS using a Fresnel-law-based model, analyzing the dependences of motion responsivity upon parameters in device structure, probing wavelength, and type of 2D material. We find that the best responsivity is achieved as the vacuum gap varies (with crystal thickness) around integer multiples of half of the probing wavelength. The optimized device thickness depends on both the type of crystal and probing wavelength. Specifically, when using 633nm He-Ne laser, the ~300nm-SiO$_2$-on-Si substrate commonly used in 2D research offers close-to-optimal motion responsivity for several 2D crystals over a wide range of thickness, provided that the oxide is fully removed underneath the 2D layer. We further show that different type of 2D layered materials exhibit different patterns in the same parameter space due to their different band structure and dielectric constants.

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11:20am **MN+2D-WeM11 NEMS on Flexible Substrates for Strain Engineering in Sensing Applications**, ***Swapnil More***, Indian Institute of Science, India

Although nanoelectromechanical systems (NEMS) utilizing 2D material are potent instruments for ultra-sensitive mass spectroscopy, the onset of nonlinearities severely reduces their dynamic range. However, strain tuning of dynamic range is possible if the strain is introduced by methods other than electrostatic gating. Here, we present a method for the fabrication of nanoelectromechanical resonators (NEMRs) from 2D materials on flexible substrate, which allows straining devices through substrate bending, which is independent of electrostatic excitation of the of the resonator. This device platform can be a basis for studying dynamic range of NEMRs as a function of strain in the resonating membrane, along with studying new novel concepts for sensors involving strain engineering. With the advent of new 2d materials having exotic strain dependent properties, strain engineering opens whole new set of opportunities for the sensing technologies employing NEMS, other than strain tunable dynamic range.

11:40am **MN+2D-WeM12 Parametric Amplification in MoS2 Drum Resonator**, ***Parmeshwar Prasad****, *N. Arora, A.K. Naik*, Indian Institute of Science, India

Transition metal dichalcogenide (TMDC) materials offer an alternative to carbon based materials, due to their unique mechanical, electrical and optical properties [1] . Molybdenum disulphide (MoS$_2$ ) is one such material which is being explored for NEMS applications. It has ultra-low mass density of 3.3 fg/µm$^2$ and high Young's modulus 0.3 TPa . Furthermore, its semi-conducting property allow its mechanical motion to be transduced electrically. NEMS devices based on 2D materials perform exceptionally well in terms of quality factor at low temperatures. Quality factors (Q) as high as $10^5$ have been observed at cryogenic temperatures[2]. However, at room temperatures quality factors are typically pegged at 100. Low quality factor of these resonators make them difficult to transduce the motion of these resonators and thus hinder applications as potential ultra-sensitive detectors. In this paper, we amplify the motion of these resonators by parametric amplification. We report enhancement of mechanical response in MoS2 drum resonator using parametric amplification and achieve ~ 10dB gain. We also show quality factor enhancement in the resonator with parametric amplification at 397 K. The signal enhancement is similar to the recently reported NEMS devices [2], However, the amplification is significantly lower as compared to the reported MEMS devices [3]. We investigate the effect of Duffing (cubic) non-linearity in the current work and show that it plays significant role in the maximum achievable gain from NEMS devices using parametric amplification. The experiments are performed using direct capacitive measurement technique on near insulating ~ 1GΩ device. This shows the ability to perform electrical capacitive actuation and detection technique in very high resistance NEMS devices.

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12:00pm **MN+2D-WeM13 Anisotropic Thermal Conductivity of Suspended Black Phosphorous Probed by Opto-thermomechanical Resonance Spectromicroscopy**, ***Arnob Islam*****, *P.X.-L. Feng*, Case Western Reserve University

Two-dimensional (2D) black phosphorus (P) exfoliated from its layered bulk crystals has attracted great attention due to its unique in-plane anisotropic properties along armchair (AC) and zigzag (ZZ) directions [1-2]. Probing the anisotropic properties in the black P is important for both exploring fundamental science and engineering device performance . Here, we employ

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* **MEMS/NEMS Best Paper Award Finalist**

2D nanoelectromechanical systems (NEMS) platform to study anisotropic thermal conductivity ($k$) of black P.

In this study, for the first time, we use thermomechanical motion with localized laser heating (Fig. 1a) (*optothermomechanical spectromicroscopy)* in combination with finite element modeling (FEM) to precisely determine anisotropic $k_{AC}$ and $k_{ZZ}$ of black P. We fabricate a black P circular drumhead resonator (thickness of $t$=~80nm and diameter of $d$=~9µm) using a dry-transfer method [3]. Before resonance measurement, polarized reflectance measurement is performed to determine the crystal orientation of the black P flake (Fig. 1b) [4]. We then employ a 633nm laser (laser power of $P$=1.6mW, spot size of 1µm) to photothermally heat up the device and interferometrically detect Brownian motion. We obtain the fundamental mode frequency at $f_{res}$=~9MHz when the laser is located on the center of the device. We move the laser spot location along AC/ZZ on the resonator, and track $f_{res}$ along the path. We find that measured $f_{res}$ values are higher when laser spot is moving in AC direction ($f_{res,AC}$) than that in ZZ direction ($f_{res,ZZ}$)(Fig. 1c) at same distance from the center. This can be attributed to anisotropic $k_{AC}$ and $k_{ZZ}$, which dictates different temperature distribution on the device as the laser is moving along AC/ZZ, providing uneven biaxial thermal expansion thus frequency shift.

We employ FEM simulation to model the coupling between thermal transport from optothermal heating and resonance characteristics of the black P drumhead resonator. By fitting the modeling to the experimental results, we are able to determine anisotropic thermal conductivities along AC/ZZ orientations ($k_{AC}$=15Wm$^{-1}$K$^{-1}$ and $k_{ZZ}$=55Wm$^{-1}$K$^{-1}$) (Fig. 1c and 1d), which are consistent with $k_{AC}$ and $k_{ZZ}$ obtained by other methods [2].

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## Nanometer-scale Science and Technology Division
## Room: 19 - Session NS+SS+SU-WeM

## Nanotechnology for Renewable Energy
**Moderator:** Robert Ilic, NIST

8:40am **NS+SS+SU-WeM3 Can "Photovoltaic" Halide Perovskites (MAPbI$_3$ & MAPbBr$_3$) be Ferroelectric?**, ***David Cahen***, Weizmann Institute of Science, Israel **INVITED**

Ferroelectricity, well-known in oxide perovskites, was suggested as possible reason for the outstanding solar-to-electrical energy conversion of MAPbI$_3$ & MAPbBr$_3$-based halide perovskite PV cells, esp. because ferroelectric domain wall conduction was thought to keep photogenerated charges separated.( à low carrier recombination rate à high photovoltage efficiency).

Contradicting e xperimental evidence, relevant to ferroelectricity, is based on structural diffraction, electric field vs. polarization plots, second harmonic generation and piezoelectricity measurements . To resolve this debate we first asked if

· the materials are pyroelectric, direct evidence for *spontaneous polarization*, a necessary condition for ferroelectricity.

· polar-domains exist in the structure, as often found in many ferroelectric materials.

Using home-grown, well-characterized single crystals, we find the cubic phases of MAPbI$_3$ (>330K) and MAPbBr$_3$ (>236K) phase to be non-polar, excluding ferroelectricity in them. The tetragonal phase of MAPbI$_3$, however, shows clear evidence of pyroelectricity when probing the potentially-polar, [001], crystallographic orientation, proving its polar nature. By adding low-temperature electric field vs. polarization and room temperature SHG studies and optical observations of polar domains, we arrive at a clear-cut conclusion that MAPbI3 is ferroelectric in the tetragonal phase. I will briefly dwell on the remaining question, i.e., "does that really matter?".

* work done by Yevgeny Rakita, Dr . David Ehre, Omri Bar-Eli, Elena Meirzadeh, Hadar Kaslasi, Yagel Peleg, with Profs. Gary Hodes, Igor Lubomirsky, Dan Oron, all from the Weizmann Inst.

9:20am **NS+SS+SU-WeM5 NSTD-Recognition Award Talk: Mixed-Dimensional Nanomaterial Heterostructures for Electronic and Energy Applications**, ***Mark Hersam***, Northwestern University **INVITED**

Layered two-dimensional (2D) nanomaterials interact primarily via van der Waals bonding, which has created new opportunities for heterostructures that are not constrained by epitaxial growth. However, it is important to acknowledge that van der Waals interactions are not limited to interplanar interactions in 2D materials. In principle, any passivated, dangling bond-free surface interacts with another via non-covalent forces. Consequently, the emerging layered 2D nanomaterials can be integrated with a diverse range of other materials, including those of different dimensionality, to form van der Waals heterostructures. This talk will explore mixed-dimensional combinations of 2D + n-D (n = 0, 1 and 3) materials, thus significantly expanding the van der Waals heterostructure concept [1]. In order to efficiently explore the vast phase space for mixed-dimensional heterostructures, our laboratory employs solution-based additive assembly [2]. In particular, constituent nanomaterials (e.g., carbon nanotubes, graphene, transition metal dichalcogenides, black phosphorus, and boron nitride) are isolated in solution, and then deposited into thin films with scalable additive manufacturing methods (e.g., inkjet, gravure, and screen printing) [3]. By achieving high levels of nanomaterial monodispersity and printing fidelity, a variety of electronic and energy applications can be enhanced including digital logic circuits [4] and lithium-ion batteries [5]. Furthermore, by integrating multiple nanomaterial inks into heterostructures, unprecedented device function is realized including anti-ambipolar transistors [6], gate-tunable photovoltaics [7], and neuromorphic memristors [8]. In addition to technological implications for electronic and energy technologies, this talk will explore several fundamental issues including band alignment, doping, trap states, and charge/energy transfer across previously unexplored mixed-dimensional heterointerfaces.

[1] D. Jariwala, *et al.*, *Nature Materials*, **16**, 170 (2017).

[2] J. Zhu, *et al.*, *Advanced Materials*, **29**, 1603895 (2017).

[3] J. Kang, *et al.*, *Accounts of Chemical Research*, DOI: 10.1021/acs.accounts.6b00643 (2017).

[4] M. Geier, *et al.*, *Nature Nanotechnology*, **10**, 944 (2015).

[5] K.-S. Chen, *et al.*, *Nano Letters*, **17**, 2539 (2017).

[6] D. Jariwala, *et al.*, *Nano Letters*, **15**, 416 (2015).

[7] D. Jariwala, *et al.*, *Nano Letters*, **16**, 497 (2016).

[8] V. K. Sangwan, *et al.*, *Nature Nanotechnology*, **10**, 403 (2015).

11:00am **NS+SS+SU-WeM10 Magnetron Sputtered Nanostructured TiO$_2$ Thin Films for Dye Sensitized Solar Cells Applications**, ***Pierre-Antoine Cormier***, *J. Dervaux*, ChIPS, University of Mons, Belgium, *Y. Pellegrin, F. Odobel,* CEISAM, University of Nantes, France, *R. Snyders*, ChIPS, University of Mons, Belgium

Among the many advantages of Dye Sensitive Solar Sells (DSSCs), their non-toxic and low cost components, their lightweight and their high performances under diffuse light and high temperatures are very interesting. DSSCs are therefore considered as a promising alternative to conventional Si and chalcogenide based solar cells. In DSSCs, the light is absorbed by dye molecules inducing an electron injection into a TiO$_2$ nanoparticles (NPs)-based photo-anode. Although this allows a high photon collection, the charge transport is limited by charge recombination at the NPs boundaries limiting the solar to conversion efficiency [1]. Many efforts have been devoted to rule this problem such as replacing NPs by nanofils, nanotubes or hierarchical nanostructured thin films which offer a direct path way to electrons [1]. We previously shown that such hierarchical structure can be obtained by reactive magnetron sputtering (RMS) at grazing incidence which allows to tune the film morphology from slanted nanoculmns, to zigzag or pillars [2].

In this work, such films were synthesized and annealed during 2h at 773 K under atmospheric pressure in order to obtain nanocolumns composed by a single anatase crystal as verified by TEM. These films were used as photo-anode in liquid DSSCs, which were characterized under simulated AM1.5 Global spectrum and 1sun illumination. Different morphologies (slanted columns, zigzag and pillars) and different thicknesses of slanted columns based films were studied. In addition, the dye grafting efficiency on these structures was evaluated by absorbance measurements performed by UV-Visible spectrophotometry.

The slanted columns-based cells present the best performances followed by zigzag and pillar based ones. This result is directly related to the corresponding specific surface area which is the highest for the slanted columns films. By increasing the thickness of the slanted films from 1.2 to 4.3 µm, the cell efficiency increases from 1.2 to 2.6 %. As the short-circuit current density also increased while the open circuit voltage was not affected, it was concluded that the critical parameter limiting the cell efficiency is the adsorbed dye density, which is enhanced for thicker films

To overcome this limitation still using thin films, the slanted columns films were impregnated by TiO$_2$ NPs (~20nm). This allows for an enhancement of the cell efficiency by 2.2% attributed to a synergetic effect between: (i) a higher dye adsorption and (ii) and the very good charge transport through the single crystalline columns.

[1] A. Hagfeldt et al. "Dye-Sensitized Solar Cells," 2010

[2] J. Dervaux et al., Vacuum, vol. 114, pp. 213–220, Nov. 2014.

11:20am **NS+SS+SU-WeM11 Spectroscopic Evolution of Halide Perovskite Growth on Graphene Oxide Surfaces for Photovoltaics**, ***Muge Acik***, Argonne National Laboratory, *G. Lee*, Ulsan National Institute of Science and Technology, Korea, *R.A. Rosenberg*, Argonne National Laboratory

High power conversion efficiency of perovskite-based solar cells offers promise for low-cost and scalable production of renewable energy. Hybrid organic-inorganic methylammonium lead halides, $MAPbX_3$ (X=I, Br, Cl)/mixed-halides ($I_{3-x}Cl_x$, $I_{3-x}Br_x$) have been reported as light harvesting layers with tunable bandgaps, long electron-hole diffusion lengths and high electron/hole mobility. Nevertheless, halide-based perovskites require *in situ* investigation for film growth mechanisms to overcome detrimental effects of incomplete lead precursor conversion, inconsistent crystallite formation/film uniformity, and weak cation-anion-solvent coordination (1). Graphene-derived hybrids has recently emerged as an ETL/HTL replacement in these devices. Graphene/perovskite structure-property relationships are, however, not well understood due to unclear chemistry at the ETL/perovskite/HTL interfaces (2). Moreover, effect of film thickness, lead content, stoichiometry control, and overlayer/underlayer morphology/composition ought to be examined for better charge transport at the graphene/perovskite interfaces. Stability factors also need to be studied for charge mechanisms to unravel device performance challenges. Indeed, underlayer ETLs ($TiO_2/Al_2O_3$) and overlayer HTLs (spiro-OMeTAD) were rarely studied with graphene. To address scalability and stability issues, we investigated degradation, nucleation and growth mechanisms in reduced graphene/graphite oxide (RGO) upon halide-based (I, Cl, Br) perovskite deposition. Chemical interactions were interpreted at perovskite/RGO interfaces for the grain size, orientation, boundaries, and surface/bulk effects using variable-temperature (≤600°C, Ar(g)) *in situ* spectroscopy (infrared absorption and micro-Raman). Controlled perovskite formation was achieved at room temperature for bromide-based perovskites resulting in improved chemical stability (vs. iodide/chloride derivative). Perovskite decomposition was observed at ≥150°C on RGO surfaces. Oxygen-induced chemical reactions occurred at ≤150°C, initiated at room temperature because of precursor interactions forming carbonyls upon perovskite deposition (3), and eliminated hydroxyls reducing GO during perovskite growth. Poor perovskite formation was observed on RGO due to varying electron affinity and reactivity of precursor halides, resulting in film degradation in air ($O_2$, $H_2O$). Film morphology was explored by SEM, XRD, XPS, AFM, and the reaction mechanisms were studied by first principles calculations that bring insights for solar cell design principles.

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11:40am **NS+SS+SU-WeM12 2D Material Laminates for Ultra-fast and Selective Molecular-scale Separation**, ***Saeed Moghaddam***, University of Florida

Due to their intrinsic properties, 2D materials have provided a unique opportunity to develop membranes with ultrafast and highly selective permeation capability. Graphene oxide (GO) is among 2D materials that has garnered significant attention in the past several years and numerous studies have been conducted on transport characteristics of its laminates. However, a comprehensive understanding of the effect of synthesis conditions on physicochemical conditions of GO that dictate transport characteristics of its laminates is lacking. In this study, the effect of oxidation conditions during the synthesis process of GO flakes on transport characteristics of GO laminates are investigated. Transport properties of the GO laminates are observed to be significantly different. It is determined that i) mean-flake size, ii) surface defects, and iii) inter-layer spacing are the key parameters.

The fundamental knowledge gained has been utilized to developed membrane separators for energy and water applications. To enhance performance of DMFCs, it was determined that at a constant oxidation level methanol permeability decreases linearly with increasing the GO mean flake size while changes in proton conductivity remain insignificant. This behavior is attributed to difference in adopted conduction pathways of protons and methanol molecules. With increasing the oxidation level, proliferation of surface defects is deductively reasoned to be the dominant factor responsible for a large increase in the measured methanol permeability. The proton conductivity is also significantly increased with increasing the oxidation level because of greater number of ion exchange sites, shortened transport pathway and increased GO flakes inter-layer spacing. The observed transport characteristics are attributed to either different adopted conduction pathways or surface mobility of protons and methanol molecules. The findings imply that the GO nanoplatelets contain atomic formations that are more selective to protons than to methanol molecules.

We have also utilized the superior water selective transport properties of GO laminates as filtration membranes for Endocrine Disrupting Compounds (EDCs) with high permeate flux rates. A layer-by-layer (L-b-L) approach was utilized to prepare thin film composite membranes with a polymer support and a few layers of GO interlinked via poly(allylamine hydrochloride) (PAH). The prepared membrane showed a fourfold increase in the permeate flux in comparison to the commercially available nanofiltration (NF) membranes. The rejection performance of the membrane was evaluated by studying the permeation of ibuprofen and a rejection rate of 75% was obtained.

## Plasma Science and Technology Division
## Room: 22 - Session PS+NS+SS-WeM

## Plasma Processing for Nanomaterials & Nanoparticles
**Moderators:** Hisataka Hayashi, Toshiba, Japan, Kazunori Koga, Kyushu University, Japan

8:00am **PS+NS+SS-WeM1 Plasma Catalysis: a Powerful Blend of the Four States of Matter**, ***Kostya (Ken) Ostrikov***, Queensland University of Technology and CSIRO, Australia **INVITED**

Plasma catalysis is a rapidly emerging multidisciplinary field at the interface of catalysis, nanotechnology, physical chemistry, materials and plasma science. Relevant applications include plasma-assisted catalytic reforming of gas mixtures into fuels, chemicals and synthesis of functional nanomaterials. Plasma-specific effects play a major role in nanoscale catalytic phenomena. The process outcomes are improved when catalysts with nanometer-scale surface features are used along with atmospheric-pressure plasmas (APPs). It is possible that plasmas and catalysts act synergistically.

I will review the APP interactions with the nanometer-size features on the surface of catalyst nanoparticles (NPs). Basic understanding of plasma-catalyst interactions is achieved through nd the effects of these modified surfaces on catalytic reactions. Nanoscale interactions of APPs with the NPs and synergistic effects are related to plasma modifications of catalyst structure and reactivity. The synergistic effects may increase the yield and selectivity of catalytic reactions of importance to chemical and energy resource industries.

The focus is on gas mixtures relevant to natural reforming or hydrogen production by water splitting. The selected nanomaterials catalyze the conversion of the above gas mixtures into higher-value products such as synthetic gas (syngas), hydrogen, fuels, etc. of demand in a variety of industrial applications (e.g., methanol production). The plasmas induce “epigenetic” modifications of catalytic materials and the plasma process parameters are customized to maximize both the conversion rates and the process gas flow, i.e., both the outcome (selectivity) and the productivity (rates) of the gas conversion.

I will discuss the most effective nanoscale plasma-surface interactions. The focus will be on surface modifications (e.g., functionalization, expression of crystal facets, changes in reactivity of near-surface atoms, oxidation or reduction states, etc.) of localized surface areas induced by the nanoscale plasma-surface interactions and chemical reactions. The plasma effects enhance reactivity of the “epigenetically” modified surface areas of the NPs. The expected effects include better adsorption, higher conversion rates of reactant species on the modified surfaces, larger surface areas for reactions, higher catalytic activity through more effective electron transfer, reduced reaction activation barriers, photon- and ion-assisted reactions, new plasma-enabled reaction pathways, etc.

8:40am **PS+NS+SS-WeM3 Vaporization of Nanoparticles in Low Temperature Plasmas**, ***Necip Berker Uner***, *E. Thimsen*, Washington University in St. Louis

Particle nucleation is a major problem that occurs in many thin film processing plasmas. The resultant “killer particles” can create defects upon deposition on the film and they can consequently decrease device functionality. A change of perspective, within the last two decades, the aptness of low temperature plasmas (LTP) for particle nucleation has been successfully exploited to synthesize monodisperse, free standing, spherical and crystalline semiconductor nanocrystals from vapor precursors. These impressive properties of particles synthesized in LTPs stem from particle charging and ion bombardment. When the particle number density is smaller than the ion density, it is proposed that the particles experience unipolar charging. The negative charge acquired by the particles suppresses coagulation and leads to uniform growth. On the other hand, ion bombardment elevates particle temperatures above the surrounding gas temperature and provides crystallinity. By using LTPs, nanocrystals of silicon, germanium, various oxides, sulfides and compound semiconductors of high quality have been produced, whereas production of metal particles were less successful, which indicates incomplete understanding.

In this study, we focus on the interaction between the plasma and metal nanoparticles. In an environment free of vapor precursors, we demonstrate that particle growth in LTPs follows a reversible path. Instead of continuous growth, ion bombardment can lead to extensive vaporization, depending on the plasma density and vapor pressure. By sending in a premade aerosol of bismuth particles through a capacitively coupled radio frequency argon plasma, we observed complete vaporization of the metal at moderate power inputs. Interestingly, at low power inputs, vaporization resulted in significant restructuring of the particle size distribution. Polydispersed size distributions were transformed into monodispersed distributions, with relatively high mass yields reaching 65%. Based on spatial Langmuir probe measurements and detailed aerosol dynamics modelling, we propose that upon exposure to different plasma densities, particles can vaporize and then the resultant vapor can either nucleate into particles or recondense on the remaining clusters, eventually leading to the modification of the size distribution. When particles vaporize completely and the vapor is conserved, the result is the conversion of a polydispersed size distribution into a monodispersed size distribution. This unusual mechanism that involves vaporization at low temperature will be detailed with further experimental observations with different materials. Methods of tuning the final size will be elaborated.

### 9:00am **PS+NS+SS-WeM4 Nanowires, Trusses and Pillars Produced by Assembly of Plasma Generated Nanoparticles**, ***Ulf Helmersson***, *S. Ekeroth, S. Askari, R. Boyd, N. Brenning*, Linköping University, Sweden

Nanoparticles generated or supplied to a plasma attains a negative potential due to the nature of the plasma. This open up interesting possibilities in synthesis and assembly of the nanoparticles creating structures in the nano- and micro-range. In this work, we use hollow cathode sputtering powered with high-power pulse to ensure close to full ionized of the source material. This promotes rapid growth of the nanoparticles to desired sizes and the negative charge makes it possibility to guide nanoparticles for assembly and collection on desired positions. This is demonstrated by attracting nanoparticles to substrate positions with a positive potential and focusing nanoparticles through a matrix of electrostatic lenses to assemble the nanoparticles into pillars. For ferromagnetic nanoparticles, we also demonstrate generation of nanowires as well as nanowires cross-linked into trusses. Since the iron nanoparticles are generated under relatively pure condition they assemble into wires without oxides in the interfaces. Nanowires and trusses assembled on conducting substrates can potentially be used as low cost large area electrodes.

### 9:20am **PS+NS+SS-WeM5 Non-Equilibrium Plasmas for Nanoparticle Synthesis: from Semiconductors to Metals**, ***Rebecca Anthony***, Michigan State University **INVITED**

Nonthermal plasmas have been increasingly popular for synthesis of nanocrystals. Generally, these flow-through reactors are radiofrequency (RF) plasmas operated at reduced pressure (2-10 Torr) into which vapor-phase precursors are entrained. The nanocrystals form following dissociation and clustering of the precursor molecules. Among the advantages offered by plasma reactors are low-temperature environment, avoidance of liquid-phase reactants, tunable nanocrystal properties via reactor parameters, and scalability. In addition, the nanocrystals can be collected as powders for post-processing, or directly impacted onto substrates in thin-film form, sidestepping the need for additional steps such as spin- or drop-casting. Combined with the solvent-free, low-temperature, all-gas-phase nature of nonthermal plasma reactors, this opens the door to direct incorporation of nanocrystals into functional layers on arbitrary substrates - without concern about solvent orthogonality or thermal susceptibility.

Here we present our work focusing on exploiting the non-equilibrium of plasma reactors for high-quality nanocrystal growth. First we discuss silicon nanocrystals for optical applications. The properties of these nanocrystals, such as size, crystallinity, and surface, can be altered in-flight using the plasma reactor parameters - and they can be inertially impacted onto a variety of substrates. These nanocrystals exhibit efficient and tunable photoluminescence, and we have deployed them in LEDs, luminescent layers on stretchable substrates, and as sensitizers for pollutant photodegradation. The non-equilibrium environment of the plasma also allows growth of even higher-melting-point nanocrystals, and we will share our work on GaN nanocrystal growth using plasma reactors. These freestanding nanocrystals are size-tunable and have excellent crystal quality despite GaN having a bulk melting temperature of 2500°C. Finally, we will discuss formation of metal nanoparticles in the plasma using an altered-geometry RF plasma with a central consumable ground electrode, working towards expanding the range of optoelectronically functional nanomaterials that can be made using nonthermal plasmas.

### 11:00am **PS+NS+SS-WeM10 Photochemical Insulator-Metal Transition in Plasma-Synthesized ZnO Nanocrystal Networks**, ***Benjamin Greenberg***, *Z. Robinson, K. Reich*, University of Minnesota, *C. Gorynski*, University of Duisburg-Essen, Germany, *B. Voigt*, University of Minnesota, *G. Nelson*, Creighton University, *L. Francis, B. Shklovskii, E.S. Aydil, U.R. Kortshagen*, University of Minnesota

Nonthermal plasma synthesis has recently emerged as a promising method for producing highly conductive ZnO nanocrystal (NC) networks. The plasma-synthesized NC surfaces are free of ligands, which enables high interparticle electron mobility. In this work, we produce ZnO NC networks using nonthermal plasma synthesis integrated with supersonic inertial impaction deposition, and we manipulate their electron transport properties with a combination of UV illumination and NC surface modification via atomic layer deposition (ALD). Specifically, we use these treatments to increase the free electron density, $n$, and the interparticle contact radius, $\rho$, and thereby induce a transition from variable range hopping to metallic transport. We determine $n$ from the NCs' localized surface plasmon resonance (LSPR) and $\rho$ from the subtle increase in the ZnO volume fraction, and we use Fourier transform IR spectroscopy (FTIR) to ascertain the underlying NC surface photochemistry.

### 11:20am **PS+NS+SS-WeM11 Elucidating Energetic Trends in Hydrocarbon Plasma Systems for Plasma-Assisted Catalysis**, ***Tara Van Surksum***, *E.R. Fisher*, Colorado State University

Plasma-assisted catalysis (PAC) has been investigated as a promising method for pollution control, specifically for conversion or removal of volatile organic compounds. The utility of PAC is severely limited by an overall lack of understanding of plasma chemistry and the reactions occurring at the plasma-catalyst interface. The present work focuses on investigating fundamental gas-phase chemistry in hydrocarbon inductively-coupled plasma systems to understand energy partitioning in PAC systems for decomposition of volatile organic compounds. We have employed broadband absorption and optical emission spectroscopies to determine rotational and vibrational temperatures ($T_R$ and $T_V$, respectively) for multiple species (e.g., CH, $C_2$) in a variety of hydrocarbon-containing plasma systems. For example, in $CH_4$ plasmas, $T_V$(CH) ranges from ~3000 to ~5000 K, whereas $T_R$(CH) generally reaches values ranging from 1000-2000 K. Energy partitioning for the same species has also been assessed when a catalytic material (e.g., flat and nanostructured $SnO_2$ and $TiO_2$, micro-structured zeolites) is placed in the plasma. In some cases, the substrate has a measureable effect on the gas-phase chemistry, whereas in others the substrate does not appreciably alter the gas-phase of the plasma. Catalytic material properties were also evaluated via surface analysis tools (e.g., X-ray photoelectron spectroscopy, scanning electron microscopy, and Fourier transform infrared spectroscopy) and will be presented in conjunction with energy partitioning data to further elucidate information on the molecular-level processes occurring at the plasma-catalyst interface. Collectively, these data aim to unravel the complex chemistry of hydrocarbon plasma systems for PAC to achieve a viable method of pollution control.

### 11:40am **PS+NS+SS-WeM12 Synthesis of Metal Nanoparticle Electrocatalysts for Fuel Cell Applications by Atmospheric-Pressure Plasma Reduction**, ***Joffrey Baneton****, Université Libre de Bruxelles, Belgium, *Y. Busby*, Université de Namur, Belgium, *W. Debouge*, Université Libre de Bruxelles, Belgium, *G. Caldarella*, Université de Liège, Belgium, *J.-J. Pireaux*, Université de Namur, Belgium, *V. Debaille*, Université Libre de Bruxelles, Belgium, *N. Job*, Université de Liège, Belgium, *M.J. Gordon*, University of California at Santa Barbara, *R.M. Sankaran*, Case Western Reserve University, *F. Reniers*, Université Libre de Bruxelles, Belgium

Nanoparticles composed of one or more metals particularly platinum (Pt) are used as electrocatalysts in hydrogen fuel cells for the cathodic reduction of dioxygen [1]. Several challenges remain in their synthesis including controlling their morphological features (e.g. size, shape, etc.), maximizing the amount of Pt exposed while minimizing the overall amount of the expensive metal, and eliminating the presence of organic capping groups or other contaminants that cover the active surface.

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* **Coburn & Winters Student Award Finalist**

Here, different atmospheric plasma devices including a microplasma and a radio-frequency (RF) plasma torch are shown to be capable of producing Pt and Pt-based alloy nanoparticles without any organic capping molecules and minimal chemical additives. The as-synthesized nanoparticles are characterized by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) to assess their chemical purity and morphology. We find that when using the microplasma to reduce a Pt precursor in solution, small and non-agglomerated Pt nanoparticles can be directly produced in liquid phase (organic or water based). By controlling the initial amount of the Pt precursor dissolved in solution and the charge injected in the system, the nanoparticle concentration can be tuned [2]. Moreover, this methodology can be applied to bimetallic alloys to reduce the amount of Pt in the electrocatalyst.

In comparison, when using a RF plasma torch, Pt nanoparticles can be produced in the solid phase by plasma reduction of a Pt precursor dispersed on the surface of a carbon support (carbon black, carbon xerogel, carbon nanotubes or graphene) [3]. A mechanism for the plasma reduction of Pt is proposed. It is shown that the size distribution of the particles, their dispersion at the surface, and their quantity in the bulk determined by inductively coupled plasma mass spectrometry (ICP-MS), can be fully controlled by the plasma and preparation parameters.

The Pt nanoparticles synthesized by either method are finally used to fabricate the cathode of a proton exchange membrane fuel cell (PEMFC) using a gas diffusion layer as a substrate. The cell performance, represented by the ratio of the electrochemically active surface area (ECSA) and the catalytic activity, which are comparable to commercial cells, will be discussed in detail.

[1] H.A. Gasteiger et al. *In*: W. Vielstich, A. Lamm and H.A. Gasteiger (eds.), Handbook of Fuel Cells – Fundamentals, Technology and Applications, Wiley, Chichester (UK), **2003**, Vol.3, p. 593.

[2] C. De Vos et al. *J. Phys. D: Appl. Phys.* (**2017**), 50, 105206.

[3] D. Merche et al. *Plasma Process. Polym.* (**2016**), 13, 91–104.

12:00pm **PS+NS+SS-WeM13 Microplasma Spray Deposition of Metal Oxide Nanostructures for Energy Applications**, ***Katherine Mackie***, *M.J. Gordon*, University of California at Santa Barbara

A general, substrate-independent method for plasma deposition of nanostructured, crystalline metal oxides is presented. The technique uses a flow-through, micro-hollow cathode plasma discharge (supersonic microplasma jet) with remote anode to deliver a highly-directed flux of growth species to the substrate. A diverse range of nanostructured materials (e.g., CuO, α-$Fe_2O_3$, and NiO) can be deposited on any room temperature surface, e.g., conductors, insulators, plastics, fibers, and patterned surfaces, in a conformal fashion. The effects of deposition conditions, substrate type, and patterning on film morphology, nanostructure, and surface coverage will be highlighted. Energy storage application examples to be discussed include NiO on carbon for supercapacitors and CuO for conversion-type Li-ion batteries. The synthesis approach presented herein provides a general and tunable method to deposit a variety of functional and hierarchical metal oxide materials on many different surfaces.

## Plasma Science and Technology Division
## Room: 23 - Session PS-WeM

## Advanced BEOL/Interconnect Etching

**Moderators:** Fred Roozeboom, TNO-Holst Centre & Eindhoven University of Technology, The Netherlands, GeunYoung Yeom, Sungkyunkwan University, Republic of Korea

8:00am **PS-WeM1 Plasma Etch Considerations for EUV Quad-layer Patterning Stacks**, ***Angélique Raley***, TEL Technology Center, America, LLC, *J.C. Shearer, I.P. Seshadri, A. De Silva, J.C. Arnold, N. Felix*, IBM Research Division, Albany, NY, *H. Cottle, A. Metz*, TEL Technology Center, America, LLC

Continued scaling in semiconductor technology nodes has seen the rise of multi patterning for several critical layers, leading to higher costs, variability, and process complexity. EUV direct print patterning can alleviate and address some of these issues. The insertion of this technology was showcased in 2016[1] by the IBM Alliance for back end of the line (BEOL) metal trenches on their 7nm device. Exploratory efforts have now shifted to enabling the second generation of EUV patterning, targeting sub-36nm pitch resolution with single exposure. In current CAR-based EUV lithography, thin photoresist is used to prevent pattern collapse defectivity in dense line-space regions. This thin photoresist requires careful engineering of the hardmask and underlayer films below to minimize selectivity burden on etch budgets. This paper will first discuss the etch process design differences between current 36nm pitch EUV patterning and what is needed for sub-36nm pitch. Secondly, we will survey several thin hardmask materials and discuss their interactions with various plasma chemistries. For each material, the impact of both gas chemistry and tuning parameter on selectivity and resist roughness will be reviewed. Finally, continuous wave plasma etch performance will be contrasted with a quasi-ALE plasma etch process[1,2] as well as other plasma etch schemes designed to widen the patterning process window and enable successful pattern transfer into a typical BEOL metal patterning stack.

This work was performed by the Research Alliance Teams at various IBM Research Facilities

[1] Xie, VLSI, IEDM, p. 2-7, 2016

[2] Cottle et al. AVS 2016 Quasi-ALE Plasma Etching of EUV Photoresist for Contact Profile Control and PR Selectivity Improvement

[3] Vinayak et al. AVS 2014 Plasma Etch Considerations for Roughness Improvements during EUV and DSA Pattern Transfer using Mid Gap CCP

8:20am **PS-WeM2 Direct Metal Etch Evaluation for Advanced Interconnect**, ***Sara Paolillo***, *F. Lazzarino, N. Rassoul, D. Wan, D. Piumi, Z. Tokei*, IMEC

For many decades, the semiconductor industry could follow Moore's law by introducing innovative device architectures, smart design, new integration and patterning concepts, better tools and new materials. While industry is almost ready for high volume manufacturing of the 7nm technology node, new approaches are constantly being tested by research centers to enable further scaling down to the 5nm and 3nm technology nodes targeting respectively a metal pitch of about 32nm and 21nm. At such aggressive pitches, the effective resistivity of damascene Cu wires increases drastically due to both surface and grain boundary scattering but also due to the need of a Cu diffusion barrier that can't be scaled down. Besides the resistivity aspect, low-k damages induced by both plasma processing and barrier deposition contribute to the low reliability performance of damascene Cu interconnects.

In this context, alternative integration schemes exploiting direct metal etch technology and alternative metals like Ru have gained interest. A semi-damascene flow for instance can advantageously be used to overcome the aforementioned challenges. It consists of opening the vias into the low-k layer and filling them with a blanket metal deposition; connection are then created into the metal layer through direct etch. The empty trenches are finally either filled with low-k or used in an air gap configuration. This concept shows many advantages: it is suitable for a barrier-less integration, it prevents low-k damage and it allows for larger metal grain size. Regarding material selection, Cu is not a viable option considering the well-known difficulties in reactive dry Cu patterning. Ru is chosen as an alternative thanks to the ease with which it can be patterned using a conventional RIE process. Moreover, Ru line resistance is expected to go below Cu line resistance at CD below ~13nm, considering a line aspect ratio of 2. A further decrease in resistance can be expected with an increase in the Ru line aspect ratio.

In this work, we study the integration of Ru as a material for interconnect wires using a semi-damascene flow. Ru lines at 32nm pitch and with an aspect ratio of at least 2 are patterned using direct RIE targeting lines of 16nm and exploring a scaling extension down to 12nm. We will compare the electrical performances of Ru lines made from 3 different integration schemes. In one case, the patterns will be obtained using EUV single print lithography and in the other two cases, a 193i lithography will be employed defining the metal lines either from the spacers in the Anti Spacer Quadruple Patterning (ASQP) approach or from the tone inverted trenches in the SAQP approach.

8:40am **PS-WeM3 Evolution of Dielectric Etchers**, ***Hiromasa Mochiki***, Tokyo Electron Miyagi Limited, Japan **INVITED**

Plasma etchers have met stringent requirements of selectivity, profile, loading and uniformity to make shrinking of device dimensions possible. To that end, plasma etchers evolved from single frequency capacitively coupled plasma (CCP) to multiple frequency CCP, high density plasma (ICP, Microwave) and remote plasma sources. CCPs have been employed in dielectric etches due to it's ability to achieve high ion energies and low dissociation rate. Single frequency CCP evolved to CCP with magnetic enhancement and decoupled CCPs with high frequency on the top electrode or on the wafer. These knobs provided independent control plasma density and ion energy. Innovation in RF engineering enabled RF power to be split in different segments of electrodes to provide uniformity control and to eliminate standing wave effects. Recently, Direct Current Superposition (DCS) has been added to CCPs to alleviate differential charging, control C/F ratio in fluorocarbon plasmas and curing of resists. In addition to etching dielectric SiO2 and low-k materials, CCPs are employed in etching hard-mask etching process. For 7nm and beyond technology, the shrinking of critical dimensions (CD) without iso-dense loading is required. To meet this requirement, in-situ ALD + Etch is used. With Fusion of Etch and ALD, CD shrink with atomic precision for various patterns, without causing CD loading is achieved. In addition, uniformly control of the CD shrinkage amount across the wafer and Line Edge Roughness Improvement are demonstrated by ALD + Etch process. Process results will be presented to elucidate etch hardware evolution.

9:20am **PS-WeM5 Etch Residue Formation and Growth on Patterned Porous Dielectrics: Angle-resolved XPS and Infrared Characterization**, ***QuocToan Le***, *E. Kesters, F. Holsteyns*, IMEC, Belgium

Porous low-k dielectrics have been commonly used in micro- and nanotechnologies since the past decade. In back-end of line interconnect, the dielectric layer is typically patterned by dry etching through a photoresist or metal hard mask using fluorocarbon-containing plasmas, followed by electroplating of Cu inside the etched patterns. Residues are always formed during the pattern etching, regardless of the hard mask type.

This study focused on the types of residues generated during, and after, the plasma patterning of TiN hard mask/ porous low-k damascene stack. The porous dielectric s used in this study were CVD organosilicate glass (OSG) with target *k*-values of 2.2 and 2.55. Stacks of Si substrate/ OSG/$SiO_2$/TiN (from bottom to top) of 45 nm ½ pitch were prepared as test vehicles. Several methods commonly used for blanket surface characterization were applied for the patterned structure under study, including contact angle, Fourier transform Infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). Using fluorocarbon-based dry etch plasma to pattern the OSG, for both 45 nm ½ pitch stacks, etch residues were detected on the TiN surface, dielectric sidewall and bottom (Figure 1, after aging, Supplemental document). The XPS F1s core-level spectra collected from the patterned OSG consisted of two main components: a sharp peak centered at ~684.6 eV corresponds to F-Ti bonds and the peak at higher binding energy (chemical shift ~3.9 eV) can be assigned to C-F bonds. In order to have further insight into the residue location, XPS spectra were collected at various take-off angles (TOA, measured with respect to the surface normal) with the beam perpendicular to the low-k lines. While the polymer-based residues (CFx) are mainly detected on trench sidewall and bottom (measured at low TOA, Figure 2, Supplemental document), the metal-based residues (TiFx) are mainly formed on the top surface (at high TOA). For the high binding energy component, the apparent chemical shift recorded at low and high TOA's is estimated to be ~0.85 eV, suggesting the presence of organometallic-type residues close to the top surface.

The effect of moisture and aging time on the density of the residues were investigated. Ti-containing residues tended to grow upon aging. The saturation level of the growth appeared to depend on the amount of the residues initially present on the surface. In terms of residue removal, the effect of a subsequent plasma treatment (post-etch treatment) and/or a wet clean on the removal of these residues was also studied.

9:40am **PS-WeM6 Etch Challenges Associated with Sub-36nm Pitch BEOL EUV Patterning**, ***Jeffrey Shearer***, IBM Research Division, *A. Raley*, TEL Technology Center, America, LLC, *A. De Silva, L. Meli, I.P. Seshadri, R.K. Bonam, N.A. Saulnier, B. Briggs*, IBM Research Division, *T. Oh*, Samsung Electronics Co. Ltd., *A. Metz*, TEL Technology Center, America, LLC, *J.C. Arnold*, IBM Research Division

The rising cost of implementing EUV lithography is often cited as a major detractor for its adoption in future semiconductor technology nodes. The ability to directly print EUV levels with a single exposure not only alleviates some of the cost of processing but also many of the process challenges associated with multiple patterning techniques. However, scaling EUV technology, notably beyond 36nm pitch, comes with its own challenges. For example, constraints on resist thickness and hardmask material choices have emerged as unique etch challenges for BEOL patterning. Both new etch chemistries and novel etch techniques, such as the implementation of quasi-atomic layer etching and DC superposition, have proven invaluable in patterning beyond 36nm pitch.

We have demonstrated capability for EUV single exposure patterning beyond 36nm pitch using both trilayer and quadlayer patterning stacks. This paper will highlight benefits and challenges of each in terms of etch development. Specifically, SiARC-based patterning stacks will be compared to organic BARC-based quadlayer stacks with various hard layers in them. The introduction of each stack material was tested at 36nm pitch before transferring to sub-36nm pitch devices. Each pitch and stack has its own set of etch considerations, and we will address their impact on pattern transfer capability, CD process window, LER/LWR, the effort and methods necessary to overcome resist scumming, line end pullback, and others. An analysis of etch parameter selection will show how defectivity can be improved for each material stack. A programmed roughness structure allows detailed LER/LWR analysis for etch process tuning. Lastly, we will discuss the benefits and drawbacks of each patterning stack and present an outlook on material selection for next-generation sub-36nm pitch architecture.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

11:00am **PS-WeM10 ALD-SiO2 Chamfer-Less-Flow for Dual Damascene Integration**, ***Xinghua Sun***, *T. Yamamura, A. Metz, P. Biolsi*, TEL Technology Center, America, LLC, *H. Nagai, R. Asako*, Tokyo Electron Limited PCDC, Japan

In the traditional back end of line (BEOL) Dual Damascene structure integration, all-in-one-etch flow has been widely applied for successful interlayer metal connection. As technical node is being scaled down to 10/7nm, ever 5nm with lower K value (2.5), via chain chamfer profiles become more and more important to chip yield. However, once via mask organic is stripped off during all-in-one etch, chamfer corner extensively exposes to trench etching plasma damage resulted from radical or ion bombardment. Therefore, chamfer corner can be etched much faster than trench, resulting in seriously rounded and chopped chamfer corner. In addition, ultra low K material can be damaged by some plasma like organic strip plasma. After the trench etch/wet clean and metallization, the rounded and chopped chamfer corner can cause electrical short, remarkably lowering yield and reliability. Regarding this point, it is a very critical goal to minimize such rounding/damage of chamfer as much as possible.

We here present an atomic layer deposition (ALD)-SiO2 chamfer-less Dual Damascene flow. In this flow, a few nanometer ALD-SiO2 film is deposited around via after via opening. The SiO2 pillar left on via sidewall plays the role to protect the chamfer corner from seriously chopping and damage while the following etching. According to different applications, this SiO2 pillar height is controllable and completely etched off while trench process. This can significantly improve the chamfer angle/profile. The ALD-SiO2 chamfer-less-flow has a few advantages. First, ALD oxide material can be uniformly deposited on via sidewall and easily etched off with trench process. Second, trench is not affected since the ALD-SiO2 is deposited before organic layer stripping. Third, it is a simple integration flow as only one extra SiO2 deposition step is added. The last one is to prevent electrical short between via chain and underneath metal, which improves the chip yield/reliability.

11:20am **PS-WeM11 Tone Reversal Technology Development Targeting Below 5nm Technology Node Applications**, ***Stefan Decoster***, *F. Lazzarino, X. Piao, N. Rassoul*, IMEC, Belgium, *Y. Fourprier*, TEL Technology Center, America, LLC, *D. Piumi*, IMEC, Belgium

For many decades, the semiconductor industry could follow Moore's law by introducing innovative device architectures, smart design, new integration and patterning concepts, better tools and new materials. While industry is almost ready for high volume manufacturing of the 7nm technology node, new approaches are constantly being tested by research centers to enable further scaling down to the 5nm technology node (N5) and below. In order to enable a number of these new integration approaches, there is a growing need for a well-understood and well-controlled tone reversal technology that consists of inverting the tonality of all structures present on the wafers, such as inverting ~20nm holes to blocks and sub-20nm lines to trenches, as well as large (micrometer-sized) structures such as alignment marks and overlay targets. The multiple Litho-Etch (LE) block patterning, the Self-Aligned Block (SAB) concept or the Direct Metal Etch (DME) approach are few examples of applications that advantageously integrate such tone reversal technology. A typical tone reversal flow consists of filling the patterns to be inverted with a material that could be either spin-coated or deposited. By means of dry etching or chemical mechanical polishing (CMP), the filling material is then thinned down to the top of the filled patterns which are finally selectively pulled out leaving the reversed patterns behind. A PECVD/ALD-type of filling would generally lead to the formation of voids between the patterns and to a low planarization performance requiring the use of an expensive CMP step that has a limited process window. Spin-coated materials are providing a good alternative to PECVD/ALD layers as they offer the possibility to achieve void-free filling and good planarization performance through material and process optimization. In this work, we focus on a fundamental understanding of the planarization properties of spin-coated materials. More specifically, the filling properties and planarization of different spin-coated materials (spin-on-glass, spin-on-carbon or spin-on-metal oxides) are screened in a selection of relevant matrix materials. By means of High Resolution Profiling, top-down and X-section Secondary Electron Microscopy the planarization properties are characterized as a function of pattern size, density and aspect ratio. Finally, the performances of the most promising tone reversal technologies are evaluated on concrete N5 and N3 applications like SAB and DME.

11:40am **PS-WeM12 Towards the Elimination of Ultra-Low *k* Ash Damage Using an *In Situ* Plasma Polymerized Film during Etch**, ***Katie Lutker***, TEL Technology Center, America, LLC

Ultra-low-*k* SiCOH films (ULK) are commonly used as an interlayer dielectric layer in the back-end-of-line. Unfortunately, as the industry moves towards new lower-*k* materials, particularly for the 7 nm node and beyond, not only does the extent of the damage caused by ash to the ULK increase, but so does the effect of damaged material on device performance. Such damage can adversely alter the feature profile and CD, RC response, and device lifetime and because of the nature of the plasma etch can be difficult to prevent. The reduction or elimination of such ash damage would facilitate the continuation of in-situ ash during the dielectric open process while opening the door to more novel integration schemes that are currently limited by the creation of a damaged layer. In order to reduce the damage, we have developed a process to deposit a plasma polymerized organic film *in-situ* during the etch process. The process utilizes a novel fluorine-free chemistry using a $C_xH_yN_z$ precursor to produce a conformal film in an etch chamber. The deposition process was optimized using patterned substrates such that the effects of the plasma ash on the sidewalls and feature bottom could be monitored and compared. Because the deposition step occurs in the etch chamber, the deposition and etch steps can be cycled such that even the feature sidewalls are constantly protected. By tuning the deposition and subsequent ash plasma parameters, the resulting damage to the ULK was significantly reduced through the use of the protecting polymer film.

12:00pm **PS-WeM13 Direct Metal Nanowire Patterning Using Ion Beam Etch**, ***Shreya Kundu***, IMEC, Belgium, *S. Dutta*, KU Leuven, IMEC, Belgium, *A. Gupta, G. Jamieson, D. Piumi, J. Boemmels, C.J. Wilson, Z. Tokei, C. Adelmann*, IMEC, Belgium

Scaling of metal lines to sub-10 nm dimensions is a pivotal driving force for progressing in the field of electronics and physics. Their fabrication by conventional lift-off/damascene approaches can be highly demanding. Some of the challenges which need to be circumvented for their creation are high resolution lithography of thinner resist and pattern transfer to form well-resolved lines/spaces. In addition, stress induced ruptures can form in the grain boundaries of the deposited metal film as the linewidth and grain size converge to similar dimensions. Here, we showcase an approach wherein we can directly pattern narrow metal lines with the use of relaxed dimension 248 nm optical lithography. Ru metal films of thicknesses ranging from 8-12 nm were deposited in a conformal way atop 300 nm wide (lines/spaces), ~7 µm long and 25 nm high patterned oxide ($SiO_2$) core. The oxide core height and the metal thickness can be varied to provide the flexibility of tuning the metal cross-sectional area. Ion beam etch (IBE) using $Ar^+$ ions was carried out to remove the film from the top and adjacent trenches of the oxide core, leaving behind long, continuous Ru lines of cross-sectional area <100 $nm^2$ along the oxide sidewalls. IBE works under the principle of physical momentum transfer (binary collision process) from the incident ions to the metal atoms which causes their eventual ejection from the substrate. Hence, unlike chemical etch, the physical etch process is not impacted by the change in grain size and grain boundaries of the metal. The cross-sectional area of the nanowires and its profile could be improved by controlling the $Ar^+$ ion accelerating voltage (50-400V) and time. TEM investigation revealed that the use of this ion bombardment based physical etch process didn't have an adverse impact on the metal crystallinity.

The Ru lines were electrically examined to estimate their performance as interconnects for advanced technology nodes. The electrical resistance yield achieved was >70%, indicating this physical etch process to be a robust method for such scientific studies. The fabrication method is not complex, compatible with the current silicon-based technology and can be extended to patterning of different metals and their alloys such as Ir, Rh amongst others.

References:

[1] L. G. Wen et al., ACS Appl. Mater. Interfaces, 2016, 8, 26119.

[2] S. Yasin, D. G. Hasko, H. Ahmed, Appl. Phys. Lett. 2001, 78, 2760.

[3] P. G. Glöersen, Journal of Vacuum Science & Technology 1975, 12, 28.

## 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.

[1] Y. Y. Peng, G. Dellea, M. Minola, M. Conni, A. Amorese, D. Di Castro, G. M. De Luca, K. Kummer, M. Salluzzo, X. Sun, X. J. Zhou, G. Balestrino, M. Le Tacon, B. Keimer, L. Braicovich, N. B. Brookes and G. Ghiringhelli, [https://arxiv.org/abs/1609.05405]

[2] H. Miao, J. Lorenzana, G. Seibold, Y.Y. Peng, A. Amorese, F. Yakhou-Harris, K. Kummer, N. B. Brookes, R. M. Konik, V. Thampy, G. D. Gu, G. Ghiringhelli, L. Braicovich, M. P. M. Dean, [https://arxiv.org/abs/1701.00022]

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.

## Scanning Probe Microscopy Focus Topic
## Room: 10 - Session SP+SS+TF-WeM

## Probing and Manipulating Nanoscale Structure
**Moderators:** Zheng Gai, Oak Ridge National Laboratory, Qiang Zou, Oak Ridge National Laboratory

8:00am **SP+SS+TF-WeM1 STM-Based Nanofabrication and Integrating Nanostructures with Clean Semiconductor Surfaces**, ***Joseph Lyding***, University of Illinois at Urbana-Champaign **INVITED**

Integrating 1D and 2D nanostructures with clean silicon and III-V semiconductor surfaces represents an interesting route towards future hybrid electronic systems. In this effort, we are exploring the integration of carbon nanotubes, graphene and graphene nanoribbons (GNRs) with clean semiconductor surfaces. A key challenge is the fabrication of 'clean' nanostructure-substrate systems. We have addressed this by developing a simple dry contact transfer (DCT) process that enables the deposition of nanostructures onto atomically clean surfaces in ultrahigh vacuum. STM imaging and spectroscopy, coupled with our atomic resolution STM-based hydrogen resist process have been used to study the interactions of carbon nanotubes, graphene and atomically precise graphene nanoribbons with silicon, GaAs and InAs substrates. In these experiments, we have observed the metallic zigzag edge state in graphene[1], carbon nanotube-substrate lattice alignment effects[2], and the electronic structure of GNRs[3]. This talk will also show a method for creating sub-5nm metal wires for contacting nanostructures[4], a SPM probe sharpening technique for producing 1 nm radii probes[5], and a technique for improving the electronic performance of carbon nanotube array transistors as well as the structural and thermal performance of CNT-based composite materials[6].

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8:40am **SP+SS+TF-WeM3 Calcium Mediates Adhesion in Reservoir Fluids**, *S.L. Eichmann*, Aramco Research Center - Boston, ***Nancy Burnham***, Worcester Polytechnic Institute

Oil powers modern economies [1]. Yet only 30% of oil is recovered from a typical reservoir [2]. The reservoirs of Saudi Arabia, which provide over 10% of the world's oil [3], are unusual . T hey are highly saline, with concentrations of up to 120,000 ppm total dissolved solids (TDS), the temperatures can exceed 100° C, and the emulsion of oil and brine is dispersed within small fissures in carbonate rock. These conditions are challenging for the unhindered diffusion of the nanoparticle tracers that are used to map an oil field from one well to the next [4]. In this study, bare and carboxyl-terminated atomic-force microscope tips and calcite surfaces acted as surrogates for nanoparticle tracers and carbonate rocks, respectively. They were immersed in three fluids: brine (120K ppm TDS), seawater (60K ppm TDS), and calcium-doped seawater (~60K ppm TDS). Surprisingly, the amount of total dissolved solids was not a good predictor of the tip-sample adhesion. Rather, specific ion effects were important; adding calcium to seawater brought the adhesion down to the ~100 pN levels of brine as compared to the ~400 pN levels of seawater . The adhesion for the carboxyl-terminated tips was greater (reaching into the nN-range) than for the bare tips, but the same trends were observed. These results can be used where fresh water for oil recovery is in short supply. The addition of calcium to seawater should mitigate nanoparticle-rock adhesion and allow more efficient diffusion of nanoparticle tracers through a reservoir, which could in turn lead to better oil recovery and help ensure a stable supply of an essential global resource.

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9:00am **SP+SS+TF-WeM4 Nanoscopy of Muscovite Mica**, ***Sampath Gamage***, *M. Howard, A. Fali*, Georgia State University, *K. Bolotin*, Free University of Berlin, Germany, *Y. Abate*, Georgia State University

Muscovite type mica is an inorganic material most commonly used as in various electronic devices. Mica also satisfies many characteristics such as excellent thermal stability, high dielectric strength, larger dielectric constant, high Q factor, and high electrical resistivity needed for organic field effect transistors (OFETs) 1-2. We use the near-field imaging and nano-FTIR techniques to investigate nanoscale absorption properties of mica exfoliated on SiO2 substrate in the frequency range of 4 – 15 μm.

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11:00am **SP+SS+TF-WeM10 Investigation of Energy Transfer and Conversion at a Single Molecule with an STM**, ***Yousoo Kim***, RIKEN, Japan **INVITED**

Excitation of molecules by light irradiation triggers various important processes including luminescence, photovoltaic effect and photochemical reactions, and detailed understanding of the molecular excited states is crucial to improve organic opto-electronic devices. Absorption spectroscopy is a powerful tool to describe the molecular excitations and the combination with emission (luminescence) spectroscopy which deals with deexcitation processes is effective to investigate the excited states. Single-molecule luminescence detection has progressed rapidly and become indispensable in quantum physics, physical chemistry, and biophysics. However, despite considerable effort and progress, absorption spectroscopy is far behind; number of molecules are still necessary to obtain an absorption spectrum. A difficulty lies in the difference between the diffraction limit of excitation light and absorption cross section of a single molecule.

Here I introduce our recent progresses in measurement of luminescence and absorption spectra and in plasmon-induced reaction at a single-molecule level using a scanning tunnelling microscope equipped with optical detection/excitation facilities.

## Surface Science Division
## Room: 25 - Session SS-WeM

## Deposition and Growth at Surfaces
**Moderators:** Kathryn Perrine, Michigan Technological University, Arthur Utz, Tufts University

8:00am **SS-WeM1 Metal Growth on and under Graphene: Morphology, Intercalation and Magnetization**, ***Michael Tringides***, Iowa State University and Ames Laboratory **INVITED**

Graphene based electronic and spintronic devices require understanding the growth of metals on graphene. Several metals (Gd, Dy, Eu, Fe,Pb ) deposited on epitaxial graphene were studied with STM, SPA-LEED and DFT. For practically all metals the growth mode is 3-d[1,2].This is a result of the low ratio of the metal adsorption to metal cohesive energy and repulsive interactions between unscreened charges at the metal-graphene interface that favor islands of small "footprint". It is an open challenge to find ways to modify the growth to layer–by–layer for high quality metal contacts and graphene applications as a spin filter. By growing Dy at low temperatures or high flux rates it is found that upward adatom transfer is kinetically suppressed and layer-by-layer is possible[3]. These results are also relevant for metal growth on other 2-d van der Vaals materials that also have weak bonding with metals and favor 3-d metal growth. Some of the grown metals are also characterized magnetically. Ex situ SMOKE nagnetization measurements on the grown Fe islands show a transition from superparamagnetic to ferromagnetic islands with coverage. XMCD measurements on Dy islands which grow with fcc(111) crystal structure (instead of the bulk hcp Dy structure) show that the islands are paramagnetic.

The graphene-metal interaction is also important for metal intercalation which provides a novel way to tune graphene's properties, besides doping. However many issues related to the intercalation process itself are poorly understood, i.e., the temperature and entry points where atoms move below graphene, different intercalation phases, their coverage, etc. SPA-LEED and STM were used to study these questions for Dy intercalation. Spot profiles of several spots (specular, 6sq(3), graphene ) are studied as function of temperature and electron energy to deduce the kinetics of intercalation and the layer where the intercalated atoms reside.

Dy nucleation experiments were performed on graphene partially intercalated with Dy. The results show that nucleation is preferred on the intercalated than on the pristine areas. Difference in doping between the two areas generates an electric field that transforms random walk to directional diffusion and accounts for the guided nucleation[4]. This can be a general method to control patterning of metallic films on graphene.

In collaboration with M. Hupalo, P. A. Thiel, M T Hershberger, D.McDougall, C.Z.Wang.

References

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8:40am **SS-WeM3 Nonequilibrium Growth of an Ordered ZnTPP Overlayer on a Ag(100)**, ***Robert Bartynski***, Rutgers, the State University of New Jersey, *P.K. Kim, S. Rangan*, Rutgers University, *C. Ruggieri*, Rutgers, the State University of New Jersey, *D. Lu*, CFN, Brookhaven National Laboratory, *S. Whitelam*, The Molecular Foundry, LBNL

Although there have been many studies characterizing the self-assembling process of organic molecules at metal surfaces, how the competition between substrate-molecule interactions and intermolecular forces impacts molecular arrangement during overlayer growth remains poorly understood. To address this question we have investigated the adsorption kinetics that leads to self-assembly of a non-equilibrium phase of zinc(II) tetraphenylporphyrins (ZnTPP) upon direct deposition on the Ag(100) surface in ultra-high vacuum (UHV).

When deposited directly onto the Ag(100) surface, the overlayer assumes a highly ordered "2+1" adsorption geometry consisting of two rows of molecules with identical registry with the surface atoms adjacent to a third row of molecules that are translated and rotated with respect to the other two rows. This structure reorganizes to the thermodynamically stable (1+1) phase upon annealing, indicating that the 2+1 geometry is a kinetically trapped growth phase.

Scanning tunneling microscopy was used to determine registry and symmetry of as-deposited and annealed ZnTPP monolayers grown in-situ on the Ag(100) surface under UHV conditions. Density functional theory (DFT) has been utilized to calculate the electronic structure and energetics of the systems, while kinetic Monte Carlo (KMC) simulations were used to model the self-assembly process. These calculations suggest that, while intermolecular interactions are primarily responsible for the thermodynamically-preferred phase, owing to the reduced number of nearest neighbors at the grow front, molecule-substrate interactions gain importance leading to the metastable 2+1 striped phase. Recent evidence pointing to the role of surface stress and molecular conformation in determining the geometry of ZnTPP on the Au(111) surface suggests that these considerations may also give rise to the non-equilibrium (2+1) phase of ZnTPP/Ag(100) [1]. This study gives insight into the fundamental mechanisms behind the self-assembly process that is not observed under multilayer deposition.

[1] Ruggieri, C., et al. Zinc (II) Tetraphenylporphyrin on Ag (100) and Ag (111): Multilayer Desorption and Dehydrogenation. *J. Phys. Chem. C.* **2016**, 120, 7575-7585.

9:00am **SS-WeM4 Growth and Motion of Liquid Alloy Droplets of Au on Ge(110)**, *B.H. Stenger, A.L. Dorsett, J.H. Miller, E.M. Russell, C.A. Gabris*, ***Shirley Chiang***, University of California Davis

The growth of Au on Ge(110) was observed with low energy electron microscopy (LEEM). The objectives of this study were to control the growth of low-dimensional nanostructures and understand the temperature induced motion of islands. Ge(110) was dosed with 0.5-5 ML of Au and heated to 850°C. During deposition, liquid eutectic alloy islands formed on the surface and grew to ~1-2 µm in width and ~2-5 µm in length, elongated along the [1,-1,0] direction due to an anisotropy in the dissolution rate of the substrate. Low energy electron diffraction (LEED) showed a transition from a (4x5) phase to a (2x1) phase immediately preceding island growth. A temperature gradient of 0.017°C/µm across the surface induced a Ge concentration gradient in the islands and diffusion of Ge through the islands from high to low temperature. Dissolution of Ge at the undersaturated high temperature end of the island and crystallization of Ge at the supersaturated low temperature end resulted in movement of the islands toward higher temperature. Smaller islands, unable to overcome pinning effects, remained stationary, while larger islands moved with velocities of 0.1-1.0 µm/s. Island velocities are consistent with a model of diffusion limited motion. Upon collision islands merged, increasing in size up to ~60 µm in width and ~100 µm in length. The direction of movement was restricted to the [1,-1,0] direction by the same dissolution anisotropy that causes island elongation during the growth process, with the exception of very large islands for which the direction was determined only by the temperature gradient. Optical microscopy confirmed that the largest islands moved from the cooler edges of the sample toward the hotter center of the sample. As the temperature decreased, the island behavior was also studied and revealed rapid island contractions as Ge crystallizes out from the islands, leaving a visible outline of the original extent of the island.

9:20am **SS-WeM5 Photodeposition of Pt Clusters on HOPG Supported TiO$_2$ Nanoparticles: Development of a Nanomaterial Model Catalyst System**, ***Jared Bruce***, *A.D. Babore, R.P. Galhenage, J.C. Hemminger*, University of California Irvine

Model heterogenous catalysts are traditionally studied using well-defined single crystal surfaces. However, industrial applications of these catalysts do not involve well – defined crystal surfaces but are comprised of colloids and other small crystallites. Development of a more representative model system, where nanomaterials and colloids of the active catalyst material are supported on an oxide nanoparticle, will enable rigorous investigation under relevant catalytic conditions.

TiO$_2$ is a stable oxide material that can be used to support an active catalyst material such as platinum. Our group has shown that physical vapor deposition can be used to create TiO$_2$ nanoparticles supported on highly oriented pyrolytic graphite (HOPG). TiO$_2$ nanoparticles are ideal for photodeposition of platinum using low concentrations of a chloroplatinate salt in aqueous conditions to control the amount of Pt deposited on the surface. Initially, the Pt deposits as a Pt (IV) oxide material as observed by X – ray photoelectron spectroscopy (XPS) and can be reduced to Pt (II) species by continued irradiation in the absence of the chloroplatinate salt in solution. Interestingly, we have not observed a complete conversion to Pt (0) and only upon heating to 400K in vacuum do we observe the presence of the Pt (0) species. We have also used temperature programmed desorption (TPD) to characterize the change in water desorption thermodynamics when Pt has been deposited on the surface of the TiO$_2$ nanoparticles. When Pt is present on the surface, there is a shift to lower temperatures in the monolayer and second layer desorption states. The relative shift is dependent on the total amount of Pt present on the surface of the TiO$_2$.

9:40am **SS-WeM6 In Vacuo Low-energy Ions Scattering Studies of ZrO$_2$ Growth by Magnetron Sputtering**, ***Marko Sturm***, *R. Coloma Ribera, R.W.E. van de Kruijs, A.E. Yakshin, F. Bijkerk*, MESA+ Institute for Nanotechnology, University of Twente, Netherlands

ZrO$_2$ thin films have applications as dielectric or passivation layer in applications as CMOS gate dielectrics and Si solar cells. Furthermore, ZrO$_2$ may be of interest as capping layer for protecting extreme ultraviolet (EUV) optics against chemical degradation processes. For these applications, it is critical that a homogeneous closed film is formed, which does not degrade the underneath layers, while the thickness is, depending on application, often restricted to a few nanometres. In this work, we studied the initial growth of ZrO$_2$ films by reactive magnetron sputtering on top of amorphous Si (a-Si), SiN$_x$ and SiO$_2$ by *in vacuo* low-energy ion scattering (LEIS). Since LEIS is selectively sensitive for the outermost atomic layer, it could be determined for which deposited thickness a closed layer was formed and how deposition parameters and surface passivation affect the sharpness of the ZrO$_2$/Si interface. The information from surface peaks of Zr, O and the a-Si substrate was compared with the so-called tail signal from particles that scatter on sub-surface Zr atoms. As example, we studied representative conditions for metallic and oxidic mode reactive magnetron sputtering. In oxidic mode, where more high energy particles are present in the deposition plasma, 3.4 nm of ZrO$_2$ was required to form a closed layer of ZrO$_2$ on Si. In metallic mode, with a lower O to Ar ratio, intermixing could be reduced by a factor 2, such that a closed film of ZrO$_2$ was formed at 1.7 nm deposited film thickness [1]. *In-vacuo* X-ray photoelectron spectroscopy (XPS) confirmed that the formation of Zr silicate at the ZrO$_2$/Siinterface was reduced in the case of metallic mode deposition. Passivation of Si by reactive deposition of a SiN$_x$ or SiO$_2$ barrier layer between the ZrO$_2$ and Si did not change the required ZrO$_2$ thickness for forming a closed layer, most likely because the Zr silicate formed during deposition already passivates the Si substrate. Thermal annealing studies in ambient atmosphere showed that 2 nm ZrO$_2$ layers deposited with metallic mode sputtering protects the underlying a-Si substrate against oxidation up to 400 °C.

[1] R. Coloma Ribera, R.W.E. v.d. Kruijs, J.M. Sturm, A.E. Yakshin and F. Bijkerk, J. Appl. Phys. **121**, 115303 (2017)

11:00am **SS-WeM10 Dihydrotetraazapentcene Growth on Alumina Thin Films and Sapphire: from the Submonolayer to nm Thick Films**, ***Anthony Thomas***, *T. Léoni, A. Ranguis, L. Masson, O. Siri*, Aix-Marseille University, France, *B. Kaufmann, A. Matkovic, M. Kratzer, C.K. Teichert*, Montanuniversität Leoben, Austria, *C. Becker*, Aix-Marseille University, France

Recently azaacenes have received increasing attention because of their semiconducting properties and their improved environmental stability as compared to acenes. Functionalizing acenes with N and NH groups may largely enhance intermolecular interactions and lead to a better order in nm-scale thin films. The interactions in those films are mediated either by H-bonding[1] or by dipole-dipole forces. In this context, the growth of Dih r ydrotetraazapentcene (DHTAP) on alumina surfaces has been studied using scanning tunneling microscopy (STM) and atomic force microscopy (AFM) at different temperatures (from 220 K to 360 K and 280 K to 390 K, respectively). For the STM measurements, DHTAP was deposited by molecular beam epitaxy in a coverage range from 0.4ML to 3.6ML on an ultra-thin Al$_2$O$_3$ film on Ni$_3$Al(111) [2]. For the AFM investigations, DHTAP (coverage range 0.4 nm to 1.7 nm) was deposited by hot-wall epitaxy on sapphire(0001) single crystal surfaces. Both, the STM and the AFM measurements show a strong dependence of the growth mode on temperature. Indeed, higher temperatures lead to fewer but bigger islands when the flux is kept constant in accordance with the common model of heterogeneous nucleation. The STM results clearly indicate a dewetting of DHTAP on the surface. It could also be shown that the emerging islands are well ordered. Two structures can be observed where the molecules are standing-up on the surface with a slight angle between their long axis and the surface normal, probably due to the steric hindering. The AFM results revealed that terraced islands and curved needle-like structures emerge above 330 K. Moreover, the islands observed by STM have step heights corresponding to upright standing molecules. Finally, the length and curvature of the needle-like structures show a clear dependence on the temperature, they are longer and more curved for higher temperatures. We try to understand how the crystalline structure of nm-sized islands overserved by STM influences the island morphology observed for thicker films by AFM.

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[1] T. Lelaidier, T. Leoni, P. Arumugam, A. Ranguis, C. Becker, O. Siri, Langmuir **30**, 5700-5704 (2014)

[2] S. Degen, A. Krupski, M. Kralj, A. Langner, C. Becker, M. Sokolowski, K. Wandelt, Surf. Sci. **576**, L57 – L64 (2005)

11:20am **SS-WeM11 Zintl Template Formation and Function during Atomic Layer Deposition Growth of Crystalline Perovskites on Ge (001)**, ***Shen Hu***, *A. Posadas, A. Demkov, J.G. Ekerdt*, The University of Texas at Austin

The growth SrTiO$_3$, SrZrO$_3$ and BaTiO$_3$ perovskites on Ge (001) has been achieved by atomic layer deposition (ALD). We find that the initial dosing of the barium- or strontium-bis(triisopropylcyclopentadienyl) precursors on a clean Ge (001) surface forms the same Zintl template as 0.5-monolayer (ML) of Ba on Ge (001) when deposited by molecular beam epitaxy (MBE).[1] The procedure to produce a Zintl template is shown in Figure 1. The Zintl templates formed by both ALD and MBE display the same X-ray photoelectron binding energy shifts for Ba 3*d*, Sr 3*d* and Ge 3*d* and both surfaces result in symmetric Ge surface dimers. The surface core level shifts indicate charge transfer from the alkaline earth metal to the Ge surface. *In-situ* reflective high energy electron diffraction images demonstrate the same 2×1-reconstructed surface after using both molecular and atomic Ba sources. High-angle annular-dark-field scanning transmission electron microscopy further confirms all ALD-grown BaTiO$_3$, SrZrO$_3$, SrHfO$_3$ and SrHf$_{0.55}$Ti$_{0.45}$O$_3$ on Ge have the similar Zintl template interface structure as MBE-grown BaTiO$_3$ on Ge. Carbon, likely in the form of dissociated ligands, binds to the Ge (001) surface during precursor dosing and some of this carbon contaminates the interface after growth.

Herein we report the role of a Zintl template formed from 0.5-ML of elemental Ba in minimizing surface carbon contamination and facilitating crystal growth. SrZrO$_3$ films are grown using ALD on the templated-surface at 225 °C using strontium-bis(triisopropylcyclopentadienyl), tetrakis(dimethylamido) zirconium (IV) and H$_2$O. The ALD chamber surfaces cannot be purged perfectly and previously-dissociated ligand products will adsorb on a clean Ge surface as shown in Figure 2 before any precursor dosing; the red line indicates that around 1 ML equivalent carbon adsorbs on the surface. An MBE-formed Zintl template blocks carbon adsorption (Figure 2). Examination of carbon levels in 2-nm and 10-nm $SrZrO_3$ films grown on bare Ge indicates the presence of carbon in the 2-nm films suggesting this initial carbon adsorption remains at the interface. Carbon levels in 2-nm and 10-nm $SrZrO_3$ films grown on 0.5-ML Ba Zintl layers cannot be detected in 2-nm and 10-nm $SrZrO_3$ films, confirming that the Zintl layer protects the surface from carbon contamination. *In-situ* XPS analysis also shows the MBE-grown Zintl template is relatively unreactive with $H_2O$; $H_2O$ reacts with adsorbed Sr and Zr precursors. The growth mechanism will be discussed during the presentation.

(Figure 1 and Figure 2 are shown in supplemental document)

[1] S. Hu et al., *J. Chem. Phys.* **146**, 052817 (2016).

11:40am **SS-WeM12 Role of the Surface Charge Density in the Surface Relaxation: The Case of Au(111)**, *M. Valbuena*, Universidad Autonoma de Madrid, *C. Quiros*, Universidad de Oviedo, *E. Salagre*, Universidad Autónoma de Madrid, *A. Oliva, M. Plaza, J. Martinez-Blanco, P. Segovia*, ***Enrique G. Michel***, Universidad Autonoma de Madrid

The formation of a surface generates in general a spontaneous contraction of the surface plane to re-establish the equilibrium (surface relaxation) [1]. There are many surfaces where the spontaneous contraction is very small or even it is an expansion instead of a contraction [2]. Interestingly, there are several prominent cases of surfaces exhibiting an anomalous expansion that also present a surface electronic state with a significant density of states [2,3,4,5]. Theoretical calculations have found [3] that the sign and magnitude of the relaxation of the topmost atomic layers of Al(100) is mainly *determined by the rearrangements of the surface state charge*. In short, the presence of a surface state increases the surface charge density, and this affects the surface relaxation. Analogous calculations show that Au(110) and Au(100) (without a high density of surface states) present a conventional surface relaxation (contraction), while Au(111) (with a prominent Shockley surface state) is characterized by an anomalous expansion [6]. These findings point towards *a strong involvement of the density of surface states in the relaxation finally observed.*

We report experimental results monitoring directly the change in surface relaxation when the surface charge in the surface state is modified. To this end, we tune the Au(111) surface state filling in a controlled way, by depositing suitable acceptor or donor molecular species. Then, we measure the surface relaxation as a function of the surface state charge, using surface x-ray diffraction (SXRD). The SXRD analysis includes the measurement of several Crystal Truncation Rods as a function of coverage of the donor or acceptor species. The results are fitted using standard procedures and provide the surface relaxation. The charge contents in the surface state is also experimentally determined from ARPES measurements of the Fermi contour for different coverages. Our results establish a direct relationship between surface relaxation and charge contents in the Au(111) surface state and shed light on the nature and deep origin of the surface relaxation process.

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12:00pm **SS-WeM13 Modeling Physical Vapor Deposition of Energetic Materials**, ***Koroush Shirvan***, MIT, *E. Forrest*, Sandia National Laboratories

The morphology and microstructure of organic explosive films formed using physical vapor deposition (PVD) processes strongly depend on local deposition conditions, especially the homologous temperature. Given the low melting points of many organic explosives, changes in surface temperature by only a few degrees can result in drastically different explosive morphology and performance. Given the difficulty of accurately measuring surface temperature during energetic material deposition, modeling may provide some insight into local conditions. This work focuses on using a multi-physics computational fluid dynamics tool, STARCCM+, to simulate PVD of pentaerythritol tetranitrate (PETN). The PETN vapor and solid phase are simulated using the volume of fluid method. The deposition fixture, copper cooling block, and assembly rotation are incorporated into the model. Implicit time-dependent simulations in 2D and 3D are performed to derive insight into the governing physics for growth of thin PETN films via PVD.

PETN is deposited at a rate of 0.8 µm/min at 142.9 °C on a 500 µm thick silicon wafer with an initial temperature of 22°C. The sublimation of PETN on the wafers is calculated to occur at a heat transfer coefficient (HTC) of 400 $W/m^2$-K. The HTC for sublimation proved to be the most sensitive parameter in determining the local surface temperature during deposition. Previous experimental studies found noticeable microstructural changes with the use of fused silica wafers of equivalent thickness in place of silicon during the PETN deposition. Effects were likely due to the change in local deposition temperature from the reduction in substrate thermal conductivity. This work confirms the effect, showing that use of fused silica substrates reduces initial wafer cool down and results in ~ 10 °C difference in the surface temperature when depositing a 500 µm thick PETN film. It was also found that the deposition surface temperature is insensitive to the cooling power of the copper block due to the very large heat capacity and thermal conductivity relative to the heat input from the PVD process. Future work will involve incorporation of local stress fields during PETN deposition and cooling.

## Sustainability Focus Topic
## Room: 5 & 6 - Session SU+AS+EM+MS-WeM

## Piezoelectrics, Thermoelectrics, and Superconductors
**Moderators:** George Nolas, University of South Florida, Kimberly Cook-Chennault, Rutgers University

8:20am **SU+AS+EM+MS-WeM2 Investigation into Novel p-type Thermoelectric Materials**, ***Dean Hobbis***, *K. Wei, G.S. Nolas*, University of South Florida

Novel thermoelectric materials are in high demand due to the ability to directly convert waste heat into electrical power, a process that has limitless applications both privately and commercially. Currently n-type thermoelectric materials have been more vastly studied than p-type and have been optimized to higher Figures of Merit (ZT). A thermoelectric module requires both n-type and p-type materials, therefore the efficiency of the module is characterized by the combination of ZT values. This means the optimization of p-type thermoelectric materials is extremely important to the commercial viability of thermoelectric technology. Furthermore, the particular synthesis method is also of importance for applications in industry. In skutterudites, for example, methods of fractional filling are typically used to improve thermoelectric efficiency by promoting phonon scattering to reduce thermal conductivity in the material, but most of the elements used as filler are electron donors. Nevertheless, Br is an electron acceptor when used as a filling atom [1]. In quaternary chalcogenides, thermal conductivity can be intrinsically low due to the crystal structure so methods to improve electrical transport is often employed through alloying and substitution on different atomic sites. Certain antimonides also possess intrinsically low thermal conductivity. Furthermore, differing processing conditions can influence the transport properties significantly, resulting in different ZT values. In this talk we present our latest work on these material systems, including new data that shows substantial improvement In ZT with composition and processing conditions.

[1] Nolas et al. *Mat. Res. Soc. Symp.* 626, **2001**, Z10.1.1

8:40am **SU+AS+EM+MS-WeM3 Thermoelectrics for Sustainable Energy Harvesting**, ***Mary Anne White***, Dalhousie University, Canada **INVITED**

Thermoelectrics can convert heat to power. The key to this process is the combined electrical (high electrical conductivity and Seebeck coefficient) and thermal (low thermal conductivity) properties. Although thermoelectrics have been used commercially for more than 50 years, new materials with higher efficiency could make their use more widespread. A large fraction of energy consumed is actually wasted as heat, so efficient conversion of this waste heat to useable power would be a great advantage to humanity. After a general introduction to thermoelectrics, this presentation will focus on improvement of thermoelectrics via sustainable approaches, including consideration of sustainability of the elements, and recent work focusing on elements with high availability.

9:20am **SU+AS+EM+MS-WeM5 Toward a Greener World: The (Re)search for Lead-Free Piezoelectrics**, ***Xiaoli Tan***, Iowa State University **INVITED**

Piezoelectricity refers to the linear coupling, in the direct effect, between mechanical stress and electric displacement, and in the converse effect, between mechanical strain and applied electric field. The proportionality constants are the piezoelectric coefficients which are equivalent between the direct and the converse effects. For the past six decades ceramics based on $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) perovskite oxides have been the workhorse of piezoelectric technology due to their excellent properties, ease of processing, and low cost. The high piezoelectric performance of PZT is primarily resulted from the intrinsic lattice distortion and the ferroelectric domain switching.

However, environmental concerns with lead have stimulated worldwide intensive efforts in the search for lead-free piezoelectric ceramics.

The research efforts on lead-free piezoelectric ceramics have been largely concentrated on three solid solution families: $BaTiO_3$-based, $(K_{0.5}Na_{0.5})NbO_3$-based, and $(Bi_{1/2}Na_{1/2})TiO_3$-based compositions. $BaTiO_3$-based ceramics exhibit excellent piezoelectric coefficients, but their applications are limited by their low Curie points (~100 ºC). $(K_{0.5}Na_{0.5})NbO_3$-based compositions possess high piezoelectric coefficients and relatively high Curie points (> 200 ºC), but have stringent requirements on the processing conditions. $(Bi_{1/2}Na_{1/2})TiO_3$-based polycrystalline ceramics develop giant electrostrains (up to 0.70%), but usually require a very high electric field.

In this presentation, an overview of the recent development in the search and research on lead-free piezoelectric ceramics will be given. Their chemical compositions, structure evolutions, and mechanisms for property optimization will be discussed. In addition, two specific investigations will be presented. The first one is on the microstructural response to poling electric fields in the $(Bi_{1/2}Na_{1/2})TiO_3–BaTiO_3$ solid solution. With the *in situ* transmission electron microscopy technique, it is directly observed that poling fields can either destroy or create morphotropic phase boundaries and the associated strong piezoelectric property. The second investigation is on the development of a giant electrostrain of 0.70% at 50 kV/cm at room temperature in $\{[Bi_{1/2}(Na_{0.84}K_{0.16})_{1/2}]_{0.96}Sr_{0.04}\}(Ti_{0.975}Nb_{0.025})O_3$. This polycrystalline ceramic with randomly oriented grains is even better than some single crystals in terms of some electromechanical properties. *In situ* transmission electron microscopy examination indicates that the giant electrostrain is originated from the reversible phase transitions under applied electric fields.

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11:20am **SU+AS+EM+MS-WeM11 Thermal Annealing Effects on the Thermoelectric Properties of Si/Si+Sb Thin Films**, ***Satilmis Budak***, *Z. Xiao, M. Curley, M. Howard, B. Rodgers, M. Alim*, Alabama A&M University

Thermoelectric devices were prepared from multi-nanolayered Si/Si+Sbthin films using DC/RF magnetron sputtering system. Thermoelectric devices were annealed at different temperatures to form quantum (nano) structures in the multilayer thin films to increase the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The prepared devices were characterized using Seebeck coefficient measurement; four probe van der Pauw measurement resistivity and the laser thermal conductivity systems. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM+EDS).

**Acknowledgement**

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

11:40am **SU+AS+EM+MS-WeM12 Critical Current by Design**, ***George Crabtree***, *U. Welp*, Argonne National Laboratory, *K. Kihlstrom*, University of Illinois at Chicago, *A. Koshelev*, Argonne National Laboratory, *A. Glatz*, Northern Illinois University, *I. Sadovskyy, W.K. Kwok*, Argonne National Laboratory **INVITED**

We introduce a new approach for rational design of superconducting critical currents, using time-dependent Ginzburg-Landau simulation to predict the critical current produced by an arbitrary mixed pinning landscape. Time dependent Ginzburg-Landau simulations automatically take into account vortex flexibility, the variation of coherence length with temperature and field, the mutual interaction of vortices and the interaction of vortices and defects. Core pinning by an arbitrary mixed pinning landscape is included by lowering the superconducting condensation energy at points, along lines and within finite nanoscale regions corresponding to specific pinning defects. We show results for several real-world cases that verify predictive ability, outline a program for unfolding the interaction of multiple pinning defects and for maximizing the critical current in targeted temperature and field ranges

*Vortices in High Performance High Temperature Superconductors*, W. K. Kwok et al., Reports on Progress in Physics. 79, 116501 (2016)

*Toward Superconducting Critical Current by Design*, Ivan A. Sadovskyy et al, Advanced Materials 28(23), 4593-4600 (2016)

This work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, as part of the Center for Emergent Superconductivity Energy Frontier Research Center and by the Scientific Discovery through Advanced Computing (SciDAC) program funded by U.S. Department of Energy, Office of Science, Advanced Scientific Computing Research and Basic Energy Science.

## 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, $\alpha_{VCC}$. Scaling of MIMCAPs for AMS applications is increasingly challenging as $C_{ox}$, $J_{leak}$, and $\alpha_{VCC}$ are all inversely proportional to dielectric thickness ($d_{ox}$). Despite its technological importance, the fundamental mechanisms responsible for $\alpha_{VCC}$ are not fully understood. It is well established that the "bulk" dielectric material has a dominant effect, where $\alpha_{VCC}$ 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 $\alpha_{VCC}$, most have focused on interfacial layer oxides (ILOs).

In this work, metals with low enthalpy of oxide formation ($\Delta H_{ox}$), 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 ($\alpha_{ECC}$) should be independent of $d_{ox}$. Instead, we find that $\alpha_{ECC}$*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, $\alpha_{ECC}$ increases with increasing $d_{ox}$, saturating for thick oxides. It has been proposed that for positive $\alpha_{VCC}$ 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 $\alpha_{ECC}$. Indeed $\alpha_{ECC}$ 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 $\alpha_{ECC}$ should aid in rapid optimization of low $\alpha_{ECC}$ 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 $5\times10^{14}$ $cm^{-3}$. The upper layer (2 µm) of n-type GaN wafer was doped with Si of $5\times10^{16}$ $cm^{-3}$ 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:

This research is supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, through its "Program for research and development of next-generation semiconductor to realize energy-saving society. This work was carried out at fluctuation free facility of New Industry Creation Hatchery Center, Tohoku University.

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.

[1] R. Dargis, A. Clark, F. E. Arkun, T. Grinys, R. Tomasiunas, A. O'Hara, and A. A. Demkov, " Monolithic integration of rare-earth oxides and semiconductors for on-silicon technology," *J. Vac. Sci. Technol. A*, 32, 041506 1-8 (**2014**).

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 ($\mu_{FE}$) 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 ($I_{on}/I_{off}$: $2 \times 10^6$, subthreshold swing: 1.8 $Vdec^{-1}$, $\mu_{FE}$: ~ 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 ≥ 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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## Thin Films Division
## Room: 20 - Session TF-WeM

### Thin Film for Photovoltaics
**Moderators:** Mariadriana Creatore, Eindhoven University of Technology, The Netherlands, Virginia Wheeler, U.S. Naval Research Laboratory

8:00am **TF-WeM1 Stable Perovskite Solar Cells by 2D/3D Interface Engineering**, ***Mohammad Khaja Nazeeruddin***, *G. Grancini, C. Roldán-Carmona, I. Zimmermann, Y. Lee,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

Metal halide perovskite solar cells (PSCs) have received global attention because of their excellent photovoltaic performance and ease of fabrication. However, much of the focus in perovskite solar cell advance has been on improved device efficiency through trial and error recipe modification. Despite the impressive photovoltaic performances, perovskite solar cells are poorly stable under operation, failing by far the requirements for a widespread commercial uptake.[1-3] Various technological approaches have been proposed to overcome the instability problem, which, while delivering appreciable improvements, are still far from a market-proof solution.[4-5] In this talk we demonstrate stable perovskite devices by engineering an ultra-stable 2D/3D $HOOC(CH_2)_2NH_3)_2PbI_4/CH_3NH_3PbI_3$ perovskite junction. The 2D/3D composite delivers an exceptional gradually organized multidimensional structure that yields 13% photovoltaic efficiency in a low cost, hole-conductor free architecture and 20% in standard mesoporous solar cells. To demonstrate the up-scale potential of this technology we fabricate 10x10 cm$^2$ solar modules by a fully printable, industrial-scale process delivering 11% efficient devices which are stable for >10,000 hours with zero efficiency loss measured under controlled standard conditions. This innovative architecture will likely enable the timely commercialization of perovskite solar cells.

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8:40am **TF-WeM3 Single-step, Atmospheric CVD of Methylammonium Bismuth Iodide Perovskite Thin Films**, *X. Chen,* Washington University in St. Louis, *Y. Myung,* Sejong University, Republic of Korea, *A. Thind, Z.N. Gao, B. Yin, B. Sadtler, R. Mishra,* ***Parag Banerjee***, Washington University in St. Louis

Synthesis of methylammonium bismuth iodide ($(CH_3NH_3)_3Bi_2I_9$) is achieved through a single step, atmospheric pressure, chemical vapor deposition (CVD) process. The precursors used are powders of bismuth iodide ($BiI_3$) and methylammonium iodide ($CH_3NH_3I$). These precursors are sublimated inside a tube furnace reactor with a well-controlled and predetermined temperature profile. The sublimated vapors are transported via Ar carrier gas to the cooler parts of the tube furnace, where simultaneous condensation and reaction between the two precursors leads to the formation of high quality $(CH_3NH_3)_3Bi_2I_9$ films on the wafer surface.

Structural and compositional information is obtained via grazing incidence X-ray diffraction (GI-XRD), SEM, TEM and XPS which confirm the $(CH_3NH_3)_3Bi_2I_9$ phase. Band-edge information is obtained via a combination of cyclic voltammetry and UV-vis spectroscopy. The band gap is revealed to be 1.9 eV. Temperature-dependent Hall measurements detect the recently observed [1] ferrielectric phase transition at ~150K via changes to the slope in the concentration vs. temperature and mobility vs. temperature curves. A room temperature electron concentration of 1.48 x $10^{19}$ cm$^{-3}$ and mobility of 7.13 cm$^2$/V.sec is obtained for $(CH_3NH_3)_3Bi_2I_9$ films with good crystallinity.

Reference:

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9:00am **TF-WeM4 Atomic Layer Deposition of $TiO_2$ Charge Recombination Blocking Layer and $SnO_2$ Electron Transport Layer for Perovskite Solar Cells**, *Y. Kuang,* Eindhoven University of Technology, Netherlands, *V. Zardetto,* Solliance Solar Research, Netherlands, *R.J. van Gils,* Eindhoven University of Technology, Netherlands, *F. di Giacomo,* Solliance Solar Research, Netherlands, *G. Lucarelli,* University of Rome Tor Vergata, Italy, *W.M.M. Kessels,* Eindhoven University of Technology, Netherlands, *T.M. Brown,* University of Rome Tor Vergata, Italy, ***Mariadriana Creatore***, Eindhoven University of Technology, Netherlands

Within the class of emerging photovoltaic technologies, perovskite solar cells have exhibited a sky-rocketing conversion efficiency above 20% in just a few years. In this contribution we will address the opportunities which atomic layer deposition (ALD) offers to perovskite solar cells [1] by highlighting the following merits: control on charge carrier transport and recombination processes at complex interfaces [2,3] and compatibility with low-temperature processing [3]. Specifically, two case studies will be presented:

· Plasma-assisted ALD amorphous $TiO_2$ (cycles consisting of $Ti(Cp^{Me})(NMe_2)_3$ and $O_2$ plasma exposure steps) has been adopted in $MeNH_3PbI_3$ perovskite solar cells in a mesoscopic configuration [2], with the purpose of suppressing charge recombination processes at the ITO/mesoscopic scaffold/perovskite interface. The superior performance of 10 nm thick ALD $TiO_2$ layers (i.e. up to 16% cell efficiency under 1000/m$^2$ illumination and 24% under indoor illumination) with respect to conventionally adopted spray pyrolysis $TiO_2$, is explained by a lower reverse dark current measured for ALD $TiO_2$. This result points out the superior blocking character of the ALD $TiO_2$ layer toward electron-hole recombination, which is also confirmed by the evaluation of the electron lifetime from open circuit voltage decay analysis. Since ALD $TiO_2$ is carried out at temperatures below 150°C, flexible perovskite solar cells built on PET/iTO substrates are also tested, exhibiting a conversion efficiency of 10.8% under indoor illumination, comparable to the one of flexible dye-sensitized solar cells and exceeding the one of flexible a-Si:H solar cells.

· Ultra-thin (15 nm) plasma-assisted ALD amorphous $SnO_2$ (cycles consisting of $Sn(NMe_2)_4$ and $O_2$ plasma exposure steps) is adopted as electron transport layer in a $Cs_x(MA_yFA_{1-y})_{1-x}Pb(I_z,Br_{1-z})_3$ perovskite solar cell in an n-i-p thin film configuration. The solar cell efficiency reaches the value of 15.9±0.5%, while the same solar cell configuration with an electron-beam deposited $TiO_2$ electron transport layer reaches an efficiency of just 10 ±0.5%. UPS analysis shows that the higher efficiency achieved by $SnO_2$ (with respect to $TiO_2$) is due to a better energy level alignment between the $SnO_2$ and perovskite conduction bands, promoting electron transport. Hole transport, instead, is efficiently blocked because of the misalignment between the $SnO_2$ and perovskite valence bands.

**References**

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[3] V. Zardetto et al., Solar Energy, accepted (2017)

9:20am **TF-WeM5 The Reaction Between Pyridine and $CH_3NH_3PbI_3$ Surface-Confined Reaction or Bulk Transformation?**, ***XiaoZhou Yu***, *H.M. Yan, Q. Peng,* University of Alabama

**Abstract**

The Methyl amine lead iodide perovskite ($CH_3NH_3PbI_3$) shows great potential in solar cells, light-emitting diodes, lasers, and chemical sensors. Base on the surface chemical properties of $CH_3NH_3PbI_3$, many chemicals with Lewis base group, for instance: pyridine, tetra-ethyl ammonium, were used to enhance the photovoltaic, optoelectronics performance and the stability in ambient environment. However, people found contradict results that Pyridine molecules not only passivate the surface $Pb^{2+}$ sites of $CH_3NH_3PbI_3$, but also to bleach and recrystallize $CH_3NH_3PbI_3$. Surface passivation demands the confinement of the reaction at the surface region but recrystallizing and bleaching require the transformation of bulk $CH_3NH_3PbI_3$. The underlying mechanism for these seemly contradicting results are not well-understood. Our results show, at 25 ºC, partial pressure of pyridine vapor is a determining factor for its reaction behaviors with $CH_3NH_3PbI_3$: one can modify just the surface of $CH_3NH_3PbI_3$ by using pyridine vapor of the pressure less than 1.15 torr, but can transform the whole bulk $CH_3NH_3PbI_3$ film with a pyridine vapor of 1.3 torr or higher. The results indicate, for the first time, that a small change of free energy of pyridine vapor (~ 0.3 kJ/mol) can cause the transition from surface-confined reaction to bulk transformation. It is interesting that in all pressure ranges, pyridinium ions is the main product from the reaction between pyridine and $CH_3NH_3PbI_3$. The bulk transformation is probably due to the formation of a liquid-like film, which increases the mobility of species to catalyze the reaction between pyridine and $CH_3NH_3PbI_3$. These findings provide a guidance for designing experiments in applying pyridine and probably other amines to functionalize and transform $CH_3NH_3PbI_3$ and other hybrid halide perovskites.

9:40am **TF-WeM6 GaN-stabilized $Ta_3N_5$ Thin Film as a Photoanode for Solar Water Splitting**, ***Taro Yamada***, *Y. Sasaki*, The University of Tokyo, Japan, *S. Suzuki*, Shinshu University, Japan, *M. Zhong*, The University of Tokyo, Japan, *K. Teshima*, Shinshu University, Japan, *K. Domen*, The University of Tokyo, Japan

Tritantalum pentanitride ($Ta_3N_5$), a visible-light absorbing material (<600 nm), was formed into a thin layer and tested as a photoelectrode in electrolytic solution under simulated solar light. By the aid of cobalt phosphate catalyst (CoPi), the electrode surface evolved $O_2$ at a substantial efficiency for photon energy conversion. By inserting a GaN layer between the catalyst and $Ta_3N_5$, the electrode exhibited an improved stability and durability for $O_2$ evolution in aqueous electrolytic solution.

The $Ta_3N_5$ film was prepared by high-temperature (1000-1300 K) nitridation of sputtered Ta film on Ta metallic substrate in $NH_3$ flow at the atmospheric pressure. Ta sputtering was performed in a RF magnetron setup with a Ta metal target at 4 Pa of purified Ar introduction pressure. The gas impurities were minimized and a trace amount of $O_2$ was introduced for sputtering. The formed Ta film is amorphous with a thickness approximately 500nm. After nitridation, the formed $Ta_3N_5$ is a transparent, orange-colored film with a visible light absorption cutoff at xxx nm. The CoPi catalyst was deposited by simulated solar irradiation in $Co(NO_3)_3$ solution in neutral phosphate buffer.

The $O_2$ evolution performance was examined in pH 13 $K_3PO_4$ buffer under potentiostatic control with a Pt counter electrode and a Ag/AgCl reference electrode. At 1.23 V vs RHE of the anodic potential, The photocurrent by a solar simulator at AM1.5G (1 $kWm^{-2}$) reached 7 $mAcm^{-2}$ or higher, however rapidly decay in 1 hour. This was due to $Ta_3N_5$ oxidation, and we introduced a GaN overlayer (thickness ~ 50 nm) by $NH_3$-nitridation of evaporated $Ga_2O_3$ layer (electron-beam heating, largely metallized). The same photoelectrochemical test exhibited a photocurrent higher than 8 $mAcm^{-2}$, lasting for more than 10 hours, with slow deactivation afterwards. Microscopic observation of the GaN layer showed fine grains (<50 nm in diameter) of GaN, blocking $Ta_3N_5$ oxidation. The faradaic $O_2$ evolution was confirmed by anther setup.

The semiconductive properties of $Ta_3N_5$ and the GaN/$Ta_3N_5$ junction are currently investigated. Both $Ta_3N_5$ and GaN in the present case are polycrystalline and contain influential amounts of impurities, reflecting in the resistivity and other transportation properties.

The photoelectrochemical performance of the present GaN/$Ta_3N_5$ electrode matches nearly 5 % of solar-to-$H_2$ energetic conversion as a free-run water photo-splitting device by assembling a with $H_2$ evolving photocathode. By improving the quality of the layers of $Ta_3N_5$ and the GaN in terms of crystallinity and purity, we can gain a good control for the performance of the photoelectrodes towards efficient solar energy recovery.

11:20am **TF-WeM11 A Viable Magnetron Sputtering Process for Thin Film CdTe Solar Cells**, ***John Walls***, *F. Bittau*, *R.C. Greenhalgh*, *A. Abbas*, *S. Yilmaz*, Loughborough University, UK

The exceptional uniformity of deposition provides magnetron sputtering with potentially important advantages for the production of thin film CdTe solar cells. For example, the thickness of the absorber layer could be reduced to ~1um saving on material cost. The uniformity is also essential for glazing applications such as power producing semi-transparent windows. Efforts to develop a viable process for the deposition of thin film CdTe solar cells by magnetron sputtering have been hampered for many years by the formation of surface blistering following the cadmium chloride activation process. Delamination of the films at the cadmium sulphide junction is often observed and catastrophic void formation within the CdTe layer and at the junction has also been reported. As a result, the conversion efficiency of sputtered devices has not matched that obtained using lower energy deposition techniques such as Close Space Sublimation or Vapour Transport Deposition. We have discovered that blistering is caused by argon trapped in the CdTe layer during the sputtering process. High Resolution Transmission Electron Microscopy reveals that argon gas bubbles are formed by diffusion during the high temperature device activation process. The bubbles then coalesce to cause surface blistering. Here we report on the development of a viable sputtering process by replacing argon with xenon as the magnetron working gas. Using xenon avoids gas bubble and blister formation. The microstructural integrity of the devices is retained resulting in increased performance of sputtered thin film CdTe photovoltaic devices.

11:40am **TF-WeM12 Hybrid Single Layer Organic Solar Cell Based on Polyvinyl Alcohol and Zinc Oxide Nanoparticles**, ***Monas Shahzad***, Forman Christian College (A Chartered University), Pakistan

Organic solar cell technology is very low cost, reliable and efficient technology. In this work, we have studied the performance of single layer hybrid organic solar cell, which is based on polyvinyl alcohol (PVA) doped with Camellia sinensis (Black Tea) solution and Zinc Oxide (ZnO) as plasmonics nanoparticles to scatter more light into active layer of solar cell. The broad absorption spectra of the composite material (PVA and tea solution) with various concentrations ranged from UV to visible region. Its energy gap was measured which allowed trapping a large portion of the incident solar light. The band gap is reduced upon the addition of Camellia sinensis (Black Tea) because the addition of Camellia sinensis (Black Tea) caused PVA to get more ordered structure. Characterization of ZnO nanoparticles using XRD and SEM confirmed the hexagonal wurtzite structure and spherical surface morphology of nanoparticles. Six solar cells were fabricated based on various concentrations of PVA doped with Camellia sinensis (Black Tea) solution using silver paste/graphite as counter electrodes, with and without ZnO nanoparticles thin film. The current-voltage (IV) characteristics curves of the fabricated organic solar cells were measured. The IV curves were studied of all soar cells that gave the following efficiencies 0.0216%, 0.0364%, 0.34%, 0.42%, 0.564 and 0.729%. The maximum energy conversion efficiency was calculated to be 0.7%, for an organic solar cell having high concentration of camellia sinensis, with ZnO nanoparticles thin film and silver paste as a counter electrode.

**Key Words:** Hybrid organic cell, polyvinyl alcohol, Camellia Sinensis, ZnO nanoparticles.

12:00pm **TF-WeM13 Phase Stability and Cation Site Distribution during Thermal Annealing of CZTS Nanoparticle-Coatings**, ***Stephen Exarhos***, *E. Palmes*, *R. Xu*, *L. Mangolini*, University of California, Riverside

$Cu_2ZnSnS_4$ (CZTS), a potential low-cost, earth-abundant absorber material, has been under intense investigation for prospective use in thin film photovoltaic (PV) devices. Its high optical absorption coefficient and variable band gap also have potential applications in other areas including photocatalysis, thermoelectrics, and energy storage. Theoretically predicted physical properties, however, have not been realized to date owing to the lack of control over chemical and microstructural heterogeneity and grain size and grain boundary chemistry. Using a modified aerosol spray pyrolysis technique, we have grown phase-pure 25 nm CZTS nanoparticles having no organic ligand contaminant. This is desirable in that grain boundary chemistry is known to degrade both optical and electrical response. Many applications demand that these nanoparticles be consolidated into relatively thick, large grain size films by means of a high temperature annealing treatment that drives impurities to interfaces thereby degrading properties. For PV applications, large grains are required to significantly reduce exciton recombination at grain boundaries. While the particles produced here do not sinter uniformly into polycrystalline thin films, we have shown that introducing a thin amorphous oxide to the surface of the particles does indeed promote uniform grain growth to create thin films with the optimal morphology for absorber layers in PV devices. The improvement is attributed to an increased retention of volatile SnS, a byproduct of CZTS decomposition, which occurs at high temperature. We have also controlled grain growth by incorporating $Na_2S$ into the film prior to annealing by means of a facile dipping technique – sodium is known to enhance grain growth in this material, though its incorporation is generally uncontrolled. Additionally, we present data from *in situ* Raman spectroscopy measurements designed to simulate the standard CZTS thin film annealing process. Using this approach, we have characterized the time/temperature effects on the vibrational spectrum of annealed CZTS films at high temperature in static variable atmospheres of sulfur vapor with and without a thin surface oxide interfacial coating. This technique is also used to monitor the cation site exchange process (copper and zinc) in the lattice that appears to be dependent on the rate of cooling following high temperature annealing.

## Vacuum Technology Division
## Room: 7 & 8 - Session VT-WeM

## Transfer and Ultraclean Systems, Particle Control, and History

**Moderators:** Jason Alfrey, Vacuum Technology, Inc., Marcy Stutzman, Thomas Jefferson National Accelerator Facility

8:00am **VT-WeM1 Applications and Challenges of UHV- and Cryo Transfer of Samples Between Independent Analytical Systems**, ***Urs Maier***, *S.A. Köster, D. von Gunten,* Ferrovac GmbH, Switzerland, *S. Yoshizawa, T. Uchihashi,* National Institute for Materials Science, Japan, *S. Rauschenbach,* Max-Planck-Institute for Solid State Research, Germany **INVITED**

To answer demanding questions in the characterization and analysis of sample surfaces a variety of high performance atomically precise methods are available. Molecular beam epitaxy (MBE), focused ion beams (FIB), electrospray ion beam deposition (ES-IBD) or even vitrification of biological samples can fabricate surfaces of great complexity with atomic/molecular precision. Similarly, analytical methods like scanning probe microscopy (SPM), electron microscopy (SEM/TEM), photo- or electron spectroscopy (e.g. XPS), low energy electron holography or secondary ion mass spectrometry (SIMS) provide spatial or chemical insight of highest precision. A combination of these methods is often desirable while these methods require a clean environment, typically ultrahigh vacuum (UHV, $10^{-10}$ mbar) and sometimes cryogenic conditions to maintain the sample in a state that allows for meaningful results.

A sample transfer with undisrupted vacuum and cryogenic conditions cannot always be achieved via a direct linkage between the instruments. More complex combinations, involving many different methods, are often impractical. The ability to transfer samples under well controlled environmental (UHV) and thermal conditions between independent analytical systems therefore greatly extends possible applications of the instrumentation.

Here we present the NexGeneration UHV suitcase system that allows to transport samples in UHV environment between instruments of even far separated facilities. The system consists of a lightweight and readily transportable vacuum chamber (the suitcase) which is actively pumped by a combination of a getter/ion pump (SAES, NEXTorr) using a battery powered controller which allow for up to 2 days off-grid operation. The transfer is facilitated via loadlocks attachable to arbitrary systems. The suitcase is of modular configuration allowing the addition of sample storage positions, adaptation to different carriers, as well as choosing from different types of sample transporters to handle the sample. Above all, a cryogenic variant of the suitcase has recently been developed, in which samples are actively cooled down to -190°C on a liquid nitrogen cooled stage situated within a thermal shield.

In the presentation we show our implementation of a sample transfer with the NexGeneration UHV suitcase system and show configurations established for different research groups. We further present data measured from samples transported within our suitcase that shows the cleanliness expected from samples that were maintained in UHV, clearly showing the capability of our system for a large variety of applications.

8:40am **VT-WeM3 Ultra-clean Sample Transportation in an EUV Exposure System**, ***Freek Molkenboer***, *N.B. Koster, A.F. Deutz, B.A.H. Nijland, P.J. Kerkhof, P.M. Muilwijk, B.W. Oostdijck, J. Westerhout, C.L. Hollemans, W.F.W. Mulckhuyse, M. van Putten, P. van der Wall, A.M. Hoogstrate, J.R.H. Diesveld, A. Abutan*, TNO, Netherlands

In 2015 TNO started the design of a new Extreme Ultra-Violet (EUV) exposure facility, called EUV Beam line 2 (EBL2). EBL2 will be a publicly accessible test facility for EUV lithography related research and qualification. The realisation of the EBL2 started at the end of Q1 2016. On December 7th 2016 the important milestone " First light" was accomplished.

EBL2 is designed to be able to load a wide range of sample types, including the EUV industry standard 6" reticles. To achieve this, all the samples are loaded using the SEMI standardised EUV dual pods.

Sample loading for the EBL2 facility starts at the Atmospheric Handler. The EUV dual pod is opened, and the Atmospheric Handler robot transfers the sample to the load lock of the EBL2 system. The Atmospheric Handler has several ultra-clean environments to limit the particle contamination on the samples.

After the load lock is evacuated to vacuum, the robot of the Vacuum Handler will transport the sample to the operator-selected module of the EBL2 system. Besides the load lock, the Vacuum Handler connects to the Expose Chamber, an XPS, and two chambers that are used for storage and cleaning of samples. In the Exposure Chamber samples can be exposed to EUV irradiation in various controllable gas environments. An XPS is available for surfaces analysis after an experiment while maintaining vacuum. The handling between the chambers is fully automated with multiple checks to ensure sample safety.

When a sample is transported to the Exposure Chamber the sample must be flipped from a horizontal loading position to a vertical mounting position. This is due to the design constraints of the EUV source and illumination module of the EBL2 system. After this flip from horizontal to vertical the sample must be positioned and clamped against the cooled Sample Chuck.

Both the flip and the clamping motions use pneumatic actuated bellows that are located inside the Exposure Chamber.

The Sample Chuck positions the sample in the EUV irradiation spot across the entire 6" reticle. The movement of the Sample Chuck is accomplished with a Hexapod that is located outside the vacuum. The vacuum barrier between the hexapod and the Sample Chuck is a large edge welded bellow.

During this presentation we will discuss our implemented design solutions for sample handling in ultra-clean vacuum. The objective of the design and implementation are to maintain the stringent vacuum and particle requirements for these kind of experiments.

9:00am **VT-WeM4 Oxidation and Contamination Monitoring Methods for Air Sensitive Materials Transfer: From Glove Box to UHV Surface Analysis**, ***Hugo Celio***, *K.B. Ohlinger*, University of Texas at Austin

The performance of lithium ion-batteries is steadily improving but there is still need for higher energy density and cycle life in consumer applications. An ex situ investigation of the composition is crucial for investigating performance issues. After a cycling period, the cathode (or anode) material is extracted from a battery coin cell under an argon environment of a glove box. However, a glove box also contains traces of $O_2$ and $H_2O$ in the 1-part-per-million range, an unknown amount of adventitious hydrocarbons and inorganic impurities. These traces of oxidants and contaminants are carried along as battery materials are transferred from a glove box to a UHV chamber for surface analysis.

An interface designed to transfer air sensitive materials from a glove box to an ultra-high vacuum (UHV) chamber for surface analysis was previously presented[1]. This interface is called an interface for pressure-to-vacuum environmental sample transfer, or IP-VEST. It is coupled to a UHV chamber equipped with X-ray photoelectron spectroscopy (XPS). The IP-VEST has a built-in method for transfer reliability. However, there is no known method to monitor the degree of oxidation to air sensitive materials from exposure to trace levels of oxidants in argon.

We selected silicon, silver, tin and lithium as a set of reference materials to monitor their surface oxidation and contamination from exposure to trace levels of oxidants, organic, and inorganic contaminants during the environmental transfer of air sensitive battery materials as described above. The preparation procedure for the reference materials is a simple mechanical step which is carried out in the glove box. We focused on evaluating the oxidation rates of clean Si, Ag, Sn and Li with respect to travel time, which is dictated by distance between the glove box and the IP-VEST/UHV chamber. At UT, five glove boxes are located within short distances of each other, entailing a preparation and travel time of less than 30 minutes. Upon arrival to the UHV chamber, the capsule, containing the air sensitive battery materials and reference materials, is coupled to the load-lock of the IP-VEST. This transfer process requires 1 hr. for samples from atmospheric argon pressure to high vacuum conditions. Based on XPS data, the surface oxidation of the reference materials significantly varies but yield a range of oxidation rates. These oxidation rates can be compared to the oxidation rates of some battery materials. The environment of the glove boxes is effectively inert for most cathode materials but insufficient for highly reactive battery materials like lithium.

[1] AVS 2015 and U.S. Patent Application Serial No. 14/445,650

9:20am **VT-WeM5 Particle Contamination Control in the Accelerator Vacuum Systems of the European XFEL**, ***Lutz Lilje***, *S. Lederer*, DESY, Germany **INVITED**

For the European XFEL accelerator vacuum about 1,5 km of vacuum system have been assembled with procedures that result in a low particulate contamination inside of the vacuum components. For this mechanical design aspects as well as cleaning and installation procedures needed to be adapted to a large variety of beam line components. An example is the development of dedicated clean rooms for the installation of components in the accelerator tunnel.

The experience with the installation is presented as well as preliminary results from the commisioning of the accelerator. An initial correlation of difficulties observed during the installation process with performance of modules will be discussed.

### 11:00am **VT-WeM10 Development, Solution of Design Issues, Final Design and Performance of an Electrostatic Triode Getter-Ion Pump, 1967-1973**, ***Paul Arnold***, MKS Instruments, Inc. **INVITED**

History of a completed commercial electrostatic triode getter-ion pump, where ion pumping and getter pumping were separated allowing preservation of the getter at UHV, will be presented. Also covered will be the solutions of combining high temperature, high voltage, high getter sublimation rate, and ultra-high vacuum in one pump design from the late 1960s. The getter was operated with active gas pumping speed as a direct function of the power to the getter and was independent of the ion pumping, allowing preservation of the getter material at UHV while maintaining full ion pumping speed. The physical electronics of a hot filament ion pump design with four pumping cells, each with dual filaments, will be shown. The successful joining and assembly of many refractory materials, some at temperatures reaching 1600 Celsius, will be described. The pump operates with electrodes at voltages up to 4000 volts in the environment of a titanium sublimation rate up to 0.02 grams per hour while maintaining adequate resistance values of the many insulators. Pumping speeds for various gasses will be displayed, along with pumpdown curves for many gasses with a gas type comparison to a sputter-ion pump from the same 1960s era. Automatic turn-on and turn-off pressure indications were provided by a heat-loss gauge with full-scale resolution of 10 millitorr. This Invited Talk is part of the AVS History Committee's endeavor to preserve and promote our vacuum technology history.

### 11:40am **VT-WeM12 The Modern View of the Vacuum**, ***H. Frederick Dylla***, American Institute of Physics

The concept of the vacuum has evolved from ancient to modern times. Ancient Greeks did not believe in the concept of vacuum-empty space in which nothing exists. With their early formulation of atom-like particles, they believed that matter was completely space filling. As civilization moved into the "Enlightenment" and the early industrial age, a practical definition of vacuum became any space evacuated to a pressure less than ambient. This is still a practical definition of vacuum in contemporary times, where state-of-the-art techniques can produce extreme vacuum levels-approaching matter densities of less than a molecule/cm$^3$. However, from the standpoint of contemporary physics, we have moved back to a view that the vacuum is not empty space devoid of content. Paul Dirac's theory of Quantum Electrodynamics, the most precisely experimentally benchmarked theory in science, portrays empty space as being filled with quantum fluctuations: virtual particle-antiparticle pairs appearing and disappearing on extremely short (Planck) time scales. The present status of cosmology research adds additional complexity to the concept of a perfect vacuum. Quantum fluctuations underpin Alan Guth's inflationary model of the universe's expansion following the primordial Big Bang. His widely accepted analysis explains the high uniformity of matter density in the observable universe-a part in 10$^4$. Quantum fluctuations in space drove an immense (10$^{28}$) expansion of the primordial universe using the latent energy in a so-called false vacuum. Over the last two decades additional observations of the universe's expansion rate, have shown that the visible components of the universe (matter and radiation) account for only about 1% of the content- 30% resides in dark matter and 70% in dark energy. Characterizing these latter two components remains on the forefront of modern physics research, and clearly a perfect vacuum is far from empty.

### 12:00pm **VT-WeM13 History of Very Thick Film and Bulk Sample Group IIIB, IVB, VB and Rare Earth Materials for Various Vacuum Applications**, ***James L. Provo***, J.l. Provo Consulting

History of Very Thick Film and Bulk Sample Group IIIB, IVB and Rare Earth

Materials for Various Vacuum Applications

James L. Provo (a

Consultant, J.L. Provo Consulting, Trinity, FL 34655-7179

Thick occluder films of hydride materials are extremely hard to produce without

flaking or cracking. This paper discusses methods of how to prepare thick films

and bulk samples (i.e., rods and wires) for many applications including accelerator

research for cancer therapy, intense neutron source, and particle-beam fusion

diagnostic beam focusing studies. These thick films ~ ( ≥ 5,000 to 15,000 nm

thick) of various hydrides are sensitive to oxidation and are easily contaminated by

improper handling. They must be specially prepared to reduce internal stresses due

to temperature variations during processing, and stresses due to hydriding and to

substrate configuration ( i.e., curved surfaces). This paper will discuss techniques

developed at the General Electric Neutron Devices Department (GEND), in Largo, FL,

in the mid-1970's to the late 1990's to produce stress free and thus flaking and crack

free samples of thick films and bulk samples. Items studied include, Er, Sc, and Ti

thick film hydrides on a Cr underlay, on various substrates, bulk rod samples (0.635

cm O.D. by 2.54 cm long) for basic material heat capacity and thermal diffusivity

studies as a function of hydride loading, Nb and V wires 10 and 20 mil O.D. by 5.08

cm long in bundles of ~30 wires for neutron vibration spectra studies and 20 mil O.D.

by 1.27 cm long Ti wires for mass spectrometer calibration studies. Film samples were

prepared by standard E-beam evaporation techniques and then non air-exposure loaded.

Bulk samples were cleaned, weighed, and then loaded with a Sievert's precise gas

quantity loading system. Special processing to accomplish flake and crack free samples,

included heating sample substrates for thick films to 450°C, evaporating at a controlled

rate of 10 nm/min.,which takes ~ 8.3 hrs. for 5,000 nm films and ~25 hrs. for 15,000

nm films, followed by non-exposure loading (i.e., leaking $D_2$ or $T_2$ gas into the loader) at a

rate of 1Torr/hr. until 50 Torr is reached, which will take ~2-days, holding at temperature

and pressure for ~ 8hrs, then cooling down at a rate of 1°C/ min.from 450°C to room

temperature. Er films are cooled to ~ 320°C, then gas is removed to the source bed to

prevent trihydride formation, before cooling to ~ (25°), which will take ~ 7.5hrs. Using

the process described, very successful results were obtained.

[*] Formerly, Principle Member of the Technical Staff at Sandia National Laboratories,

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## 2D Materials Focus Topic
## Room: 16 - Session 2D+EM+MN+NS-WeA

## 2D Device Physics and Applications
**Moderator:** Humberto Gutierrez, University of South Florida

2:20pm **2D+EM+MN+NS-WeA1 Capacitance-voltage Characteristics of Graphene-gate MOS Devices: The Effect of Graphene Quantum Capacitance**, ***Ruixue Lian***, *A. Ural*, University of Florida

There has been significant research interest in graphene for electronics applications, due to its good electrical conductivity, high optical transparency, mechanical flexibility, and two-dimensional structure. However, the potential of graphene as a channel material replacing silicon is limited due to the absence of a bandgap. On the other hand, graphene is an excellent candidate as a transparent, conductive, and flexible electrode for electronic and optoelectronic devices.

Unlike conventional metals, whose Fermi level is typically pinned at the surface, the Fermi level and hence workfunction of graphene can be tailored by electrostatic gating, chemical doping, or surface engineering. As a result, graphene is also a promising candidate as the gate electrode in metal-oxide-semiconductor (MOS) devices, particularly when transparency or workfunction tunability is a requirement.

In real graphene sheets, charged impurities cause electron-hole puddles and random local electrostatic potential fluctuations (statistically described by a Gaussian distribution), which leads to a modified density of states (DOS). In this work, using this modified DOS, we numerically compute the quantum capacitance of graphene as a function of the graphene electrostatic potential at different temperatures and strengths of the potential energy fluctuations. We compare the exact results to various approximations made in the literature when fitting experimental data. We find that the largest discrepancy between the exact results and the approximations occurs near the Dirac point.

In capacitance-voltage (C-V) characterization of graphene-gate MOS devices, what is measured is not the quantum capacitance versus the graphene potential, but the total gate capacitance versus the gate voltage. We numerically compute the gate voltage as a function of the graphene potential and the resulting C-V characteristics at different temperatures, strengths of the potential energy fluctuations, and equivalent oxide thicknesses. We also consider the effect of series and parallel parasitic impedance to the overall shape of the C-V curves. Furthermore, we numerically compute the full C-V characteristics at different values of the equivalent oxide thickness, silicon doping density, and Dirac voltage of graphene. Finally, we fit our recent experimental C-V data with these theoretical calculations to extract the strength of the potential energy fluctuations and the parasitic impedances.

These results provide important insights into the effect of the graphene quantum capacitance on the C-V characteristics of MOS devices and the potential of graphene as a gate electrode in future MOS technology.

2:40pm **2D+EM+MN+NS-WeA2 *in-situ* Electrical Characterization of Surface Functionalization and Gate Dielectric Deposition Processes on 2D Transition Metal Dichalcogenides Transistors**, ***Antonio T. Lucero***, *J.B. Lee, L. Cheng, H.S. Kim, S.J. Kim, J. Kim*, University of Texas at Dallas

Two-dimensional transition metal dichalcogenide (TMD) materials are a subject of intense research for use as future, low-power semiconductors. The successful fabrication of TMD based transistors requires a scalable dielectric deposition process. Atomic layer deposition (ALD) is commonly used to grow high-k gate dielectrics, though deposition of thin, pin-hole free dielectrics is challenging due to the chemically inert basal plane of most TMD materials. To overcome this limitation, surface functionalization processes have been developed to improve ALD nucleation.

In order to elucidate the effects of surface functionalization and subsequent ALD on the electrical characteristics of TMD transistors we use an *in-situ* electrical characterization system to measure the electrical properties of TMD transistors at various steps during the deposition process. $MoS_2$ backgated transistors are loaded into an ultra-high vacuum (UHV) cluster tool where samples can be transferred under UHV conditions between various chambers. The cluster tool is equipped with a thermal ALD chamber, a hollow cathode plasma enhanced ALD chamber, a plasma enhanced chemical vapor deposition chamber, and a UHV electrical probe station. Results for ozone, nitrogen radical, and nitrogen plasma functionalization will be presented. The effect of surface dipoles, precursor adsorption and coverage, and nucleation during the ALD process will be discussed as they relate to the electrical characteristics of the device.

This work was supported by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, and by NRF (No. 2015M3D1A1068061) in Korea. We thank TMEIC for providing the ozone generator and nitrogen radical generator used in this work.

3:00pm **2D+EM+MN+NS-WeA3 High-K Gate oxide by Low Temperature ALD Technique for 2D Materials and Inert Metal Surfaces**, ***Il Jo Kwak***, *J.H. Park*, University of California at San Diego, *S. Fathipour, A. Seabaugh*, University of Notre Dame, *C.S. Pang, Z. Chen*, Purdue University, *A.C. Kummel*, University of California at San Diego

2D materials such as TMDs(Transition Metal Dichalcogenides), Graphene and BN have attracted great attention as new channel materials for future devices due to their excellent electronic and optical properties. For such devices, sub nanometer thick and defect free gate oxide is an essential part. However, due to the inert surface of the materials, high K oxide such as $Al_2O_3$ and $HfO_2$ selectively nucleates on defect sites or step edges. Therefore, for successful integration, preparation of uniform and insulating gate oxides are a matter of importance. In this study, $Al_2O_3$ was deposited on 2D materials surface by low temperature ALD using trimethylaluminum(TMA) and $H_2O$ without any seeding layer or surface treatments. Using short purge time between two precursor pulses at 50C, a CVD component was induced to provide uniform nucleation sites on the surface. The CVD component generates subnanometer AlOx particles[s1] [file:///C:/Users/kwak1/Downloads/2017_AVS_abstract_bilayer_oxide.docx#_msocom_1] on the surface which provide uniform nucleation sites. In order to obtain lower EOT layer, 10 cycles of $Al_2O_3$ ALD was deposited at 50C as a seeding layer and 40 cycles of $HfO_2$ ALD was deposited with Tetrakis(dimethylamido )hafnium (TDMAH) and $H_2O$ at 250C. The same oxide was deposited on a SiGe substrate to compare the oxide characteristics. After ALD, MOSCAPs were fabricated to measure electrical properties. AFM measurement revealed that uniform and defect free oxide layers were nucleated on the surfaces. Capacitance-voltage measurement showed that Cox of the bilayer oxide was 2.5 uF/cm2 and the gate leakage current of the oxide was about $10^{-5}$ A/cm$^2$ which was comparable to the oxide on a SiGe substrate. Identical bilayer oxide layer was deposited on a dual gated $WSe_2$ FETs . Top gate oxide leakage of the device was about $10^{-6}$ A/ cm2. In order to assess the quality of the oxide, a benchmarking study of current density versus EOT of 2D semiconductor FET devices and Si based devises was investigated. The study showed that record-low EOT (1.2 nm) and leakage current ($10^{-8}$ μA/ μm$^2$) comparable to the best Si devices with $La_2O_3$ gate oxide by Iwai *et al* was achieved by the WSe2 FET. This technique was also applied to initiate nucleation[s2] [file:///C:/Users/kwak1/Downloads/2017_AVS_abstract_bilayer_oxide.docx#_msocom_2] on inert metal surfaces which are important for logic memory devices including selectors. Using the bilayer oxide, insulating oxide was prepared on Au electrodes of a MOSFET device. The leakage current of the oxide was as low as $10^{-7}$ A/ cm$^2$.

3:20pm **2D+EM+MN+NS-WeA4 Exploration and Comparison of Optoelectronic Properties of $MoS_2$ Monolayers with Multilayer Flakes and $Mo_xW_{1-x}S_2$ Ternary Compounds**, ***Sourav Garg***, *J. Waters, A. Mollah, S. Kim, P. Kung*, University of Alabama

2D transition metal dichalcogenide (TMDC) semiconductors, including $MoS_2$, $WS_2$, and more recently ternary compounds, exhibit exceptional structural, electrical and optical properties that make these materials of great interest for nano-optoelectronic devices. For example, unlike graphene, TMDCs have a bandgap, which has the remarkable characteristic of becoming direct when the material is in monolayer form, while it is indirect when the material is composed of multiple layers.

Here, we report the synthesis of monolayer $MoS_2$, $WS_2$, ternary $Mo_xW_{1-x}S_2$ ternary compounds and $MoS_2$/$WS_2$-based heterostructures, by chemical vapor deposition (CVD) process at temperatures in the range 950-1000 C, without the use of seeds to avoid contamination. The material was extensively characterized using micro-Raman spectroscopy, micro-photoluminescence, and electron microscopy.

Using such large area CVD grown materials, large-area $MoS_2$ photoconductive detector devices were fabricated using conventional photolithography to realize of interdigitated metal fingers. The electrical and spectral photoresponse from monolayer and multilayer $MoS_2$ have been compared, in terms of responsivity and specific detectivity. The monolayer devices exhibited high photoconductive gain and detectivity near $10^{12}$ Jones, which was also found to be higher than in the case of multilayer $MoS_2$ devices. The rise and decay time of passivated monolayer devices was investigated and shown to be much faster than the unpassivated devices.

4:40pm **2D+EM+MN+NS-WeA8 Dielectric Properties of Carbon Nanomembranes prepared from aromatic Self-Assembled Monolayers investigated by Impedance Spectroscopy**, ***Paul Penner***, *E. Marschewski, X. Zhang,* Bielefeld University, Germany, *T. Weimann, P. Hinze,* Physikalisch-Technische Bundesanstalt, Germany, *A. Beyer, A. Gölzhäuser*, Bielefeld University, Germany

Carbon nanomembranes (CNMs) are two-dimensional materials made by cross-linking self-assembled monolayers (SAMs) of aromatic molecules via low energy electron irradiation. Previous study of molecular junction incorporating SAMs and CNMs of oligophenyl thiols has been carried out by using conical eutectic Gallium-Indium (EGaIn) top-electrodes[1] and conductive probe atomic force microscopy (CP-AFM). Here we investigate the dielectric properties of pristine SAMs and CNMs with an EGaIn top electrode by impedance spectroscopy. Analysis and comparison of the tunneling resistance and capacitance density of pristine and cross-linked SAMs revealed a thickness dependent capacitance associated with the monolayer as well as a thickness independent capacitance. We adopted an equivalent circuit to take into account the contribution of the interfacial capacitance as well as the oxide layer of the EGaIn top electrode. The obtained tunneling decay constant remains unaffected after electron irradiation, which exhibits a value of about 0.5 Å$^{-1}$ for both systems. A determination of dielectric constants of SAMs and CNMs from the impedance spectra will also be analyzed and discussed. Furthermore we characterize stacks of CNMs sandwiched with graphene and other 2D materials.

[1] P. Penner, X. Zhang, E. Marschewski, et. al, J Phys Chem C 2014, 118, 21687.

5:00pm **2D+EM+MN+NS-WeA9 2D Crystals for Next-Generation Ultra Energy-Efficient Electronics**, ***Kaustav Banerjee***, University of California at Santa Barbara **INVITED**

I will highlight the prospects of two-dimensional (2D) materials for innovating energy-efficient transistors, sensors, and interconnects targeted for next-generation electronics needed to support the emerging paradigm of the *Internet of Things*. More specifically, I will bring forward a few applications uniquely enabled by 2D materials and their heterostructures that have been demonstrated in my lab for realizing ultra-energy-efficient electronics. This will include the world’s first 2D-channel band-to-band tunneling transistor that overcomes a fundamental power consumption challenge in all electronic devices since the invention of the first transistor in 1947 (Nature 2015), as well as a breakthrough interconnect technology based on doped-graphene-nanoribbons, which overcomes the fundamental limitations of conventional metals and provides an attractive pathway toward a low-power and highly reliable interconnect technology for next-generation integrated circuits (Nano Letters 2016). I will also bring forward a new class of ultra-sensitive and low-power sensors as well as area-efficient and high-performance passive devices, both enabled by 2D materials, for ubiquitous sensing and connectivity to improve quality of life.

## 2D Materials Focus Topic
## Room: 15 - Session 2D-WeA

## Properties and Characterization of 2D Materials
**Moderator:** Tien-Ming Chuang, Academia Sinica, Taiwan

2:20pm **2D-WeA1 Multi-scale Mechanics of Graphene Oxide**, ***Changhong Cao***, *M. Daly, C.V. Singh, Y. Sun, T. Filleter*, University of Toronto, Canada

The mechanical behavior of graphene oxide is length scale dependent: orders of magnitude different between the bulk forms and monolayer counterparts. Understanding the underlying mechanisms plays a significant role in their versatile application. A systematic multiscale mechanical study from monolayer to multilayer, including the interactions between layers of GO, can provide fundamental support for material engineering. In this talk, an experimental coupled with simulation approach will be introduced studying the multiscale mechanics of graphene oxide (GO).

GO is a layered nanomaterial comprised of hierarchical units whose characteristic dimension lies between monolayer GO (0.7 nm 1.2 nm) and bulk GO papers (≥ 1 μm). Mechanical behaviors of monolayer GO and GO nanosheets (10 nm- 100 nm) were comprehensively studied by our group. Monolayer GO was measured to have an average strength of 24.7 GPa, orders of magnitude higher than previously reported values for GO paper and approximately 50% of the 2D intrinsic strength of pristine graphene. The huge discrepancy between the strength of monolayer GO and that of bulk GO paper motivated the study of GO at the intermediate length scale (GO nanosheets). Experimental results showed that GO nanosheets possess high strength in the gigapascal range. Molecular Dynamic simulations showed that the transition in the failure behavior from interplanar fracture to intraplanar fracture was responsible for the huge strength discrepancy between nanometer scale GO and bulk GO papers. Additionally, the interfacial shear strength between GO layers was found to be a key contributing factor to the distinct mechanical behavior among hierarchical units of GO. The understanding of the multiscale mechanics of GO is transferrable in the study of other 2D materials.

2:40pm **2D-WeA2 Modification of Density of States in Iron Chloride Intercalated Epitaxial Graphene with Electric Bias**, *K.D. McAllister, A.P. Sharma,* Clark Atlanta University, *K. Shepperd, E.H. Conrad,* Georgia Institute of Technology, ***Michael Williams***, Clark Atlanta University

Epitaxial semi-metallic graphene on the carbon face of silicon carbide has mixed phase AA and AB stacking orders. Iron chloride intercalated graphene is characterized, by contrast, with AA stacking order. The high electronegativity of the iron chloride spacing layers between the graphene bi-layer results in hole-doping of the graphene. Ultraviolet photoemission spectroscopy is used to investigate the electronic structure modifications of stage-1 and stage-3 iron chloride intercalated bi-layer graphene with the application of an external electric field normal to the surface. The dominant features of the study are the modification of the work function and the density of states with the applied electric field and staging order of the intercalant. In particular, the p-type carriers of the stage-1 system are switched to n-type behavior with increasing field strength in agreement with recent models.

3:00pm **2D-WeA3 Anisotropic MoS$_2$ Nanosheets Grown on Self-Organized Nanopatterned Substrates**, *FrancescoBuatierdeMongeot. Buatier de Mongeot*, ***Carlo Mennucci***, Università di Genova, Italy, *C. Martella, E. Cinquanta, A. Lamperti*, IMM-CNR, Agrate Brianza (MB), Italy, *E. Cappelluti*, Istituto dei Sistemi Complessi (ISC)-CNR U.O.S. Sapienza Roma, Italy, *A. Molle*, IMM-CNR, Agrate Brianza (MB), Italy

Manipulating the anisotropy in 2D nanosheets is a promising way to tune or trigger functional properties at the nanoscale. Here, a novel approach is presented to introduce a one-directional anisotropy in MoS2 nanosheets via chemical vapor deposition (CVD) onto rippled patterns prepared on ion-sputtered SiO2 /Si substrates. The optoelectronic properties of MoS2 are dramatically affected by the rippled MoS2 morphology both at the macro- and the nanoscale. In particular, strongly anisotropic phonon modes are observed depending on the polarization orientation with respect to the ripple axis. Moreover, the rippled morphology induces localization of strain and charge doping at the nanoscale, thus causing substantial redshifts of the phonon mode frequencies and a topography-dependent modulation of the MoS2 workfunction, respectively [1].

Additionally the uniaxial morphological modulation of the MoS2 nanosheets induces a strong dichroism in their optical extinction spectra which is particularly pronounced in correspondence to the C-exciton.

This study paves the way to a controllable tuning of the anisotropy via substrate pattern engineering in CVD-grown 2D nanosheets.

[1] C.Martella et al. Adv. Mater. 2017, 1605785

3:20pm **2D-WeA4 The Potential for Fast van der Waals Computations for Layered Materials using a Lifshitz Model**, ***Yao Zhou***, *L.A. Pellouchoud, E.J. Reed*, Stanford University

Computation of the van der Waals (vdW) interactions plays a crucial role in the study of layered materials. The adiabatic-connection fluctuation-dissipation theorem within random phase approximation (ACFDT-RPA) has been empirically reported to be the most accurate of commonly used methods, but it is limited to small systems due to its computational complexity. Without a computationally tractable vdW correction, fictitious strains are often introduced in the study of multilayer heterostructures, which, we find, can change the vdW binding energy by as much as 15%. In this work, we employed for the first time a defined Lifshitz model to provide the vdW potentials for a spectrum of layered materials orders of magnitude faster than the ACFDT-RPA for representative layered material structures. We find that a suitably defined Lifshitz model gives the correlation component of the binding energy to within 8–20% of the ACFDT-RPA calculations for a variety of layered heterostructures. Using this fast Lifshitz model, we studied the vdW binding properties of 210 three-layered heterostructures. Our results demonstrate that the three-body vdW effects are generally small (10% of the binding energy) in layered materials for most cases, and that non-negligible second-nearest neighbor layer interaction and three-body effects are observed for only those cases in which the middle layer is atomically thin (e.g. BN or graphene). We find that there is potential for particular combinations of stacked layers to exhibit repulsive three-body van der Waals effects, although these effects are likely to be much smaller than two-body effects.

4:20pm **2D-WeA7 Tip Enhanced Optical Spectroscopy: A Unique Tool to Address Nanoscale Heterogeneity in 2D Materials**, ***Andrey Krayev***, AIST-NT Inc., *M. Chaigneau*, Horiba Scientific, France, *V. Zhizhimontov*, *A.E. Robinson*, AIST-NT Inc

Raman spectroscopy has proved to be an indispensable tool for characterization of both carbon-based 2D materials, such as graphene or graphene oxide, and TMDCs, providing information on: number of layers, distribution of defects, type of structure and (in case of TMDCs) excitonic behavior. Despite the wealth of the information Raman spectroscopy can provide about the structure of 2D materials, its spatial resolution is limited to approximately 300-500nm, depending on the wavelength of the excitation laser; in many cases this is insufficient for precise characterization of spatial distribution of the variations of structural and the related electronic and optoelectronic properties. Hyperspectral imaging using tip enhanced optical spectroscopy (TEOS), which includes tip enhanced Raman spectroscopy (TERS) and tip enhanced photoluminescence spectroscopy (TEPL), can dramatically improve the spatial resolution of both Raman and PL optical microscopy, providing this much-needed sensitivity.

TERS characterization of graphene and graphene oxide, both pristine and functionalized, reveals a dramatic increase in Raman response at folds and wrinkles in the flakes, as well as over the patterns imprinted in the flakes using an ultrasharp single crystal diamond probe. Interestingly, the wrinkles in graphene oxide flakes exhibit increased conductivity compared to flat areas of the flake, a rather unexpected discovery; as graphene oxide in its normal state is a dielectric, increased thickness of the material might have been expected to result in worse conductivity.

TERS and TEPL analysis of as-grown $WS_2$ demonstrated significant heterogeneity of the flakes. In an approximately 100nm-wide band adjacent to the flake edges we see both decreased, blue-shifted intensity of the photoluminescence and also increased intensity of the TERS signal; this can be attributed to decreased density of the charge carriers in the vicinity of the edges resulting in increased efficiency of Raman scattering and decreased concentration of trions, which have red-shifted PL relative to regular uncharged exitons.

TERS and correlated surface potential imaging of the $WS_2$ flakes exfoliated to gold revealed significant nanoscale (from tens to low hundreds of nanometer) variations in intensity of the major Raman bands across the flake. A high resolution map of the photoluminescence distribution extracted from the TERS map of the $WS_2$ flake clearly delineates that portion of the flake that is single layer. Correlation of the TERS hyperspectral image Raman band intensity with the distribution of surface potential may be diagnostic of TMDC doping level and of the exact sign of the charge carriers.

4:40pm **2D-WeA8 Lithium-Free Covalent Chemical Functionalization of Two-Dimensional Molybdenum Disulfide**, *X.S. Chu, A. Yousaf, D.O. Li, A.A. Tang, A. Debnath, D. Ma, A.A. Green,* Arizona State University, *E.J.G. Santos,* Queen's University Belfast, UK, ***Qing Hua Wang***, Arizona State University

Two-dimensional transition metal dichalcogenides like molybdenum disulfide ($MoS_2$) are generating significant excitement due to their unique electronic, chemical, and optical properties. Chemical functionalization is crucial for tuning their properties for use in many applications. Previous methods to covalently functionalize the basal planes of TMDCs require using harsh lithium compounds for intercalation, exfoliation, and phase change from semiconducting to metallic. Here, we demonstrate the direct covalent functionalization of unmodified semiconducting $MoS_2$ using aryl diazonium salts without lithium treatments. Our approach preserves the structure and semiconducting nature of $MoS_2$, results in covalent C-S bonds, and is applicable to $MoS_2$ derived from mechanical exfoliation, chemical vapour deposition, and liquid phase dispersion. We use density functional theory including van der Waals interactions to determine the reaction mechanism, and support it by scanning probe microscopies. The flexibility of this covalent chemistry is exploited to tether active proteins to $MoS_2$, suggesting future biological applications.

5:00pm **2D-WeA9 Spatially Resolved Modification of Graphene's Band Structure by Surface Oxygen Atoms**, *C. Harthcock, A. Jahanbekam, Y. Zhang,* ***David Y. Lee***, Washington State University

We report the spatially resolved modification of the topography and electronic properties of monolayer graphene by low dosage of atomic oxygen in the *nm*-scale. Using an ultra-high vacuum scanning tunneling microscope, we show that surface O-atoms, even at a low coverage of O/C = ~1/150, form random surface distributions and clusters of various sizes. Using scanning tunneling spectroscopy, oxygen adsorbates are observed to be *p*-type dopants, which leads to site-dependent partial and full band modifications up to a gap of few hundred meV. The degree of band gap opening and the number of O-atom induced charge-holes per area are inversely proportional to the distance between the position at which each STS spectrum is collected and the location of the nearest adsorbate. However, the number of holes contributed per oxygen atom was found to be a site-independent constant of 0.15±0.05. For a small population of adsorbates taller than 4Å, the graphene energy bands are no longer resolved; instead STS measurements show very spatially localized but high density of states over a wide energy range, which indicates sole tunneling contribution from the cluster of electron-rich O-atoms and a complete decoupling from the graphene bands

5:20pm **2D-WeA10 Enabling Atmospheric Pressure Photoelectron Imaging and Spectroscopy using Graphene**, *H.X. Guo,* National Institute of Standards and Technology, *E. Strelcov,* NIST Center for Nanoscale Science and Technology / University of Maryland, *A. Yulaev,* University of Maryland, ***Ivan Vlassiuok***, Oak Ridge National Laboratory, *A. Kolmakov*, NIST Center for Nanoscale Science and Technology

We report on recent progress in ambient pressure XPS (APXPS) spectroscopy and electron microscopy of liquid and gaseous samples enabled by electron transparent and molecular impermeable graphene membranes. Single and bilayer graphene membranes are sufficiently transparent to few hundred eV photoelectrons generated by synchrotron or laboratory x-ray sources what makes this experimental platform to be an inexpensive alternative to current differentially pumped APXPS systems. We demonstrate the capabilities of this approach on model liquids and electrochemical cells using a wide array of spectroscopy (AES, XPS, NEXAFS) and imaging (SEM, PEEM) techniques. We also discuss the limitations of this approach and lines of its future development

5:40pm **2D-WeA11 Direct Write Mask Free Fabrication of Semiconductor 2D Architectures on Different Substrates using Aqueous Inks**, ***Irma Kuljanishvili***, *D. Alameri, R. Dong,* Saint Louis University, *L.E. Ocola*, Argonne National Laboratory

Low dimensional semiconductor materials with different sized band-gaps such as 2D atomic crystals, for example WS2 or MoS2 layered van der Waals materials, or 1D nanowires (NWs) and nanoribbons such as ZnO, or semiconducting carbon nanotubes (CNTs), have drawn significant attention due to their unique physical, chemical, mechanical properties, and other just to name a few. Low dimensional materials when assembled in vertical or lateral arrangements often lead to the largely enhanced properties, and new functionalities. While the preparation of layered architectures usually involves multi-step fabrication processes it also relies on mask assisted lithographic processes.

Here we present controlled selective preparation of 1D and 2D nanostructures of MoS2, WS2 and ZnO in the variety of geometric assemblies by employing parallel direct write patterning (DWP) of aqueous ink precursors on substrates at predefined locations. In a two-step process (1st patterning and 2nd growth) our unconventional fabrication approach enables simple and flexible production of hetero-structures and other architectures based on "mix and match" principle in precisely controlled fashion. Location specific synthesis of materials also provides access to as-grown interfaces and rapid testing of materials quality, crystallinity and chemical composition which was confirmed by various characterization methods (Raman Spectroscopy, PL, AFM, XRD etc)

Acknowledgement

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6:00pm **2D-WeA12 Band Gap Tuning of MBE Grown $WSe_2$ via Solution Treatment of Ammonium Sulfide $(NH_4)_2S$ and Ozone ($O_3$)**, ***Jun Hong Park***, Institute for Basic Science (IBS), Ewha Womans University, Republic of Korea, *I.J. Kwak,* University of California at San Diego, *A. Rai, S.K. Banerjee,* University of Texas at Austin, *A.C. Kummel*, University of California at San Diego

Transition metal dichalcogenides (TMDs) have been extensively studied because of their unique electronic and optical properties. In addition, having the non-zero band gap, they can be directly integrated in logic devices. However, it is of crucial importance to tune the band gap and Fermi level positions of TMDs effectively to enhance the ON/OFF current ratio. In this study, the band gap of $WSe_2$ was engineered using a $(NH_4)_2S$ solution and a gaseous $O_3$ treatment. Prior to the chemical treatments, the surface of MBE (molecular beam epitaxy) grown $WSe_2$ was studied using STM (scanning tunneling ,microscopy). Large grains of $WSe_2$ about 100 nm were observed. The band gap of monolayer (ML) $WSe_2$ was about 2.1 eV in STS (scanning tunneling spectroscopy), consistent with previous STM studies. A bare $WSe_2$ sample was emerged in ammonium sulfide solution (40% $(NH_4)_2S(aq)$) at 300K. Afterward, the sulfur treated (ST) $WSe_2$ sample was transferred to a UHV scanning tunneling microscopy (STM) chamber to observe the effect of the treatment on the band gap. The STM imaging revealed that new electronic states were generated by ST across the entire $WSe_2$ surface, with asymmetric bias dependence. In STS, band gap of the ST $WSe_2$ was reduced to 1.2 eV, while Fermi level was pinned near the valence band. A $WSe_2$ field effect transistor (FET) was fabricated to show the effect of ST on electrical properties. Electrical measurement showed that ST of monolayer $WSe_2$ transistors increased ON states current by two order of magnitude in the p-branch, while ON state current in n -branch was increased by an order of magnitude which is consistent with the $(NH_4)_2S$ decreasing the band gap and inducing p-type doping. The band gap was also tuned by ozone ($O_3$) treatment at room temperature. A MBE grown $WSe_2$ was inserted in a vacuum chamber. $O_3$ gas was prepared by UV lamp excitation of a continuous $O_2$ flow into the chamber at 300 K for 2 min. After dosing $O_3$ gas for 2 min, the band gap of the $WSe_2$ was about 1.3 eV, while Fermi level was near conduction band indication (n-type). As exposure time of $O_3$ increased to 6 min, the band gap of ML $WSe_2$ was decreased to 1.1eV and the formation of WOx was observed on the ML terraces. Therefore, $O_3$ had the opposite behavior of $(NH_4)_2S$ since $O_3$ treatment maintained n-type doping while shrinking the band gap.

## Applied Surface Science Division
## Room: 13 - Session AS+2D+NS+SA-WeA

## 2D, 3D and nD Imaging of Surfaces, Buried Interfaces and Nanostructures

**Moderators:** Michael Brumbach, Sandia National Laboratories, Kathryn Lloyd, DuPont

2:20pm **AS+2D+NS+SA-WeA1 Laser-SNMS Imaging of Organic and Biological Systems in Two and Three Dimensions.**, ***Bonnie June Tyler***, *A. Pelster, M. Heeger, H.F. Arlinghaus*, Universität Münster, Germany

The introduction of commercial large argon gas cluster ion sputter sources has enabled routine molecular depth profiling and 3D imaging of organic materials with ToF-SIMS. 3D molecular imaging has been demonstrated for a wide variety of organic and biological systems. Despite these advances, sensitivity and quantitation continue to limit applications of the technique for many important systems such as pharmaceuticals. Laser post-ionization of sputtered neutral species is one potential solution to the problems of both low sensitivity and matrix effects.

In this work, we have compared ToF-SIMS and Laser-SNMS for 2D and 3D imaging of several organic systems, including biological samples, pharmaceuticals, and polymeric materials [1-3]. Sample analysis and sputtering were performed using combinations of $Bi_3^+$ and $Ar_n^+$ ions. Laser post-ionization was performed using either a 157 nm excimer laser or a 195 nm excimer laser. For organic molecules, superior results are obtained using the shorter wavelength laser at lower power density whereas higher power density with the longer wavelength laser is superior for elemental analysis. Increases in ion yield of as much as 4 orders of magnitude have been observed for both elemental and molecular species.

ToF-SIMS and Laser-SNMS show complementary strengths. For high intensity ion signals, ToF-SIMS allows for faster data acquisition. Laser-SNMS, on the other hand, reduces artefacts from topography and matrix effects and enhances measurement efficiency. Higher efficiency reduces the amount of matter that must be sputtered to obtain a given signal, which facilitates measurement of lower concentrations with higher ultimate spatial resolution.

[1] Nees, R.et al., Biointerphases, 2016. 11(2): p. 02A305.

[2] Pelster, A., et al., Analytical Chemistry, 2016. 88(19): p. 9638-9646.

[3] Pelster, A., et al., Biointerphases, 2016. 11(4): p 041001.

2:40pm **AS+2D+NS+SA-WeA2 Distribution of Surfactants and Polymer in a Coating using GCIB-SIMS**, ***Michaeleen Pacholski***, *Z. Qu, W. Ouyang*, The Dow Chemical Company

Water-based coatings are commonly composed of a latex polymer with additional formulation ingredients such as surfactants, defoamers, etc. The distribution of the additives can have a large role in product performance affecting properties such as adhesion, gloss, water whitening, cohesion, etc. Using GCIB-SIMS profiling the distribution of the additives throughout a film can be shown to relate to the particle size and expected film formation theoretical results. The data from this study show, for the first time, that polymer, surfactant and salts can be monitored as a function of film depth with superior sensitivity and specificity to previous literature studies.

3:00pm **AS+2D+NS+SA-WeA3 Correlation of Morphological and Hyperspectral Characterization Techniques for Nanoelectronic and Energy Applications**, ***Jean-Paul Barnes***, *A. Priebe, G. Goret, I. Mouton, A. Grenier, G. Audoit, P. Bleuet, Y. Mazel, E. Nolot*, Univ. Grenoble Alpes, CEA, LETI, France, *S. Legendre, A.L. Tempez*, Horiba France S.a.s., France, *R. Estivill, M. Juhel*, STMicroelectronics, France, *S. Duguay, F. Vurpillot, D. Blavette*, Normandie Univ, UNIROUEN, INSA Rouen, CNRS, Groupe de Physique des Matériaux, France **INVITED**

The integration of a growing variety of materials in increasingly complex structures drives the need to correlate characterization techniques. In this presentation we will discuss the advantages of correlating pairs of techniques such as focused ion beam-time of flight-secondary ion mass spectrometry (FIB-TOF-SIMS) and X-ray computed nanotomography (CNT); atom probe tomography (APT) and electron tomography (ET); and TOF-SIMS depth profiling and plasma profiling time-of-flight mass spectrometry (PPTOFMS).

FIB-TOF-SIMS tomography extends the capacity of TOF-SIMS instruments to analyze large heterogeneous samples of several tens of microns in size as well as porous samples or those with strong surface topography. Standard depth profiling is often not possible as the depth scale information is rapidly lost in such samples. Examples include copper pillars used in 3-D integration in nanoelectronics and solid oxide fuel cells (SOFCs) which have a complex porous multilayer (sandwich) structure. Whilst FIB-TOF-SIMS provides unique information on the sample chemical composition, there may be morphological artefacts such as curtaining. These may be identified and corrected by analyzing the sample beforehand by X-ray CNT in an SEM. We have developed a method to analyze the same object by both techniques by using novel sample preparation protocols [1].

The correlation of morphological with hyperspectral data can also be applied to APT and ET. APT is increasingly used for the analysis of semiconductor devices because of its unique ability to measure composition in 3D at the atomic scale with high sensitivity. However the APT data sets are often distorted and care must be taken in quantifying composition. The morphological information obtained from analyzing the APT tip beforehand by ET can be used to optimize the parameters when reconstructing the APT data.

PPTOFMS is a rapid depth profiling technique that uses a plasma to etch away the sample and analyze the composition as a function of depth. Unlike SIMS based techniques, the ionization takes place in the plasma and the ratio of ions extracted from the plasma is directly representative (within a factor of 2-3) of the sputtered sample composition. However, the sensitivity and depth resolution are worse than for TOF-SIMS. Combining PPTOFMS with TOF-SIMS depth profiling enables the standard-free quantification and rapid sample screening capabilities of the PPTOFMS to be combined with the sensitivity and high depth and lateral resolution of TOF-SIMS [3].

[1] A. Priebe et al. Ultramicroscopy. 173 (2017):10-13.[2] A. Grenier et al APL 106, 213102 (2015). [3] A. Tempez et al., J. Vac. Sci. Technol. B (2016) 34

4:20pm **AS+2D+NS+SA-WeA7 Insights into Corrosion and Radiation Damage Processes Through 2D and 3D Imaging at the Nanoscale**, ***Karen Kruska***, *D.K. Schreiber, D.J. Edwards, Z. Zhai, M.J. Olszta, I. Arslan, M.A. Conroy, C. Wang, R.J. Kurtz, S.M. Bruemmer*, Pacific Northwest National Laboratory **INVITED**

There is an increasing demand for characterization of materials for nuclear reactors with advanced microscopy techniques. Intelligent materials selection requires a fundamental mechanistic understanding of environmental and irradiation damage processes at the nanoscale.

Current and future nuclear power generating systems require materials that can withstand extreme environments. Long-term resistance to environmental degradation is critical for light water reactors as evidenced by stress corrosion cracking concerns in structural alloys for both primary and secondary systems. Resistance to radiation damage further challenges material selection in current and advanced reactors with unique issues for plasma facing components in tokamak-style fusion energy systems where materials must tolerate extended neutron (14 MeV) and $He^+$ ion (3.5 MeV) irradiation at extreme temperatures (up to 1300 K). Accumulation of metallic fission products in LWR fuels may cause cracking and has been linked to cladding erosion.

2D analytical electron microscopy techniques have and continue to provide key insights into the evolution of local microstructure and chemistry. More recently, these traditional 2D imaging techniques have been complemented by novel 3D imaging methods, including serial sectioning using a focused ion beam, electron tomography and atom probe tomography. When paired with 2D imaging methods, the 3D microscopy provides deeper insights into the hierarchy of the degradation and damage processes, improved statistical relevance and a greater sensitivity to highly localized effects that were not apparent from 2D imaging alone. Going one step further, dynamic processes (such as oxidation and vacancy injection) can be directly imaged by in situ and operando techniques in transmission electron microscopy. Each technique has its own set of strengths and weaknesses, and in this talk we will emphasize how combining these complementary techniques provides a more comprehensive understanding of material degradation than could be obtained from any individual imaging method.

5:00pm **AS+2D+NS+SA-WeA9 XPS Spectroscopic Imaging of 2D-Materials**, ***Olivier Renault***, CEA-Leti, France, *H. Kim*, EPFL, France, *D. Ferrah*, UCI, France, *N. Fairley*, Casa Software, France, *M. Gay*, CEA-Leti, France, *M. Frégnaux*, UVSQ, France, *A. Kis*, EPFL, France

The recent advent of two dimensional semi-conducting materials of the post-graphene era, such as transition-metal dichalcogenides (TMDs- such as MoS$_2$, WSe$_2$, …) has amplified the need for advanced analytical diagnostics. One of the main issues to tackle are directly related to the atomically-thin character of the samples, first concerning the low elemental concentrations and second, the invasive character of most of the characterization techniques implemented. As a photon-probe technique, XPS has a key role to play in the analysis of TMDs but highly sensitive and versatile microscopic capabilities are needed: this is because the physics of TMDs, notably the indirect-to-direct band gap transition in the monolayer limit, requires spatially-resolved information not only on the chemical composition but also on the electronic band structure. Short analysis times are required because a screening of these properties depending on processing conditions (at the material or the device level) is needed. PEEM-based instruments are the only class of XPS microscopes able to offer both type of analysis. In this presentation, we will review recent studies of 2D materials using XPEEM for chemical imaging and *k*PEEM for band structure imaging, with a particular emphasis on instrumental requirements (excitation source, transmission and detection) and post-processing of the 3D spectroscopic image data sets. The examples will range from graphene doping [1] and cleaning [2], to single layer MoS$_2$ [3-4], including also novel materials and 2D heterostructures.

This work was performed at the Platform For Nano-Characterization of CEA-MINATEC.

[1] H. Kim, O. Renault *et al*., *Appl. Phys. Lett*. **105**, 011605 (2014).

[2] M. Frégnaux, O. Renault *et al*., Surf. Interface Anal. **2016**, 48, 465-469.

[3] D. Ferrah, O. Renault et al., Surf. Interface Anal. **2016**, 48, 451-455.

[4] H. Kim, M. Frégnaux, A. Kis, O. Renault, *et al*., *Phys. Rev.* B **34**, 081401 (R) (2016).

5:20pm **AS+2D+NS+SA-WeA10 Carboxylic Acid Headgroups – Towards a New Standard in SAMs**, ***Anna Krzykawska***, Jagiellonian Univeristy, Poland, *J. Ossowski, T. Żaba, P. Cyganik*, Jagiellonian University, Poland

Self-assembled monolayers (SAMs) prepared from biphenyl-substituted molecules chemisorbed on the Ag(111) substrate via an -SH or -COOH headgroup were characterized using scanning tunneling microscopy (STM), infrared reflection absorption spectroscopy (IRRAS), and X-ray photoelectron spectroscopy (XPS). The objective of this work was to determine which of these headgroups, -SH or -COOH, will provide better 2D ordered SAMs. Importantly, to make such comparison valuable, i.e., to correlate the reduction in the concentration of surface defects with the particular headgroup, we need to compare the two systems, which are chemical analogues, and it would be desired that both systems form SAMs of similar packing density. Only under such conditions can the difference in intermolecular interactions in both systems be minimized to determine the role of headgroup bonding to the substrate in the 2D structural ordering of the resulting SAMs. Our results[1] obtained for monolayers meeting the above criteria show that SAMs with carboxylic headgroups can form, at room temperature and within a very short time of just a few minutes well-ordered 2D structures on Ag(111) with surprisingly large domains. In contrast, the thiol analogue formed at the same temperature reveals poor 2D ordering, with approximately 30 times smaller structural domains. Importantly, this pronounced difference in 2D ordering is observed despite the approximately 300 times longer incubation process of the thiol analogue. We also demonstrate that formation of the thiol analogue at elevated solution temperature (60°C) can significantly increase the size of its domains, which is, however, still approximately 5 times smaller in comparison to the carboxylic analogue formed at room temperature. Moreover, the structure of the carboxylic analogue on Ag(111) also shows better 2D order compared with the former data obtained for the thiol analogue SAMs formed on the Au(111) substrate at room temperature. Only the formation of thiol analogue SAMs at elevated solution temperature (60°C) on the Au(111) substrate with 300 times longer formation time provides comparable 2D ordering to that obtained at the room temperature for the carboxylic analogue SAMs on the Ag(111) substrate.

Our results indicate, therefore, that SAMs based on carboxylic head group can be considered an interesting alternative for the curren t standard based on the sulfur headgroups, particularly when 2D ordering, SAM fabrication time and stability in the ambient conditions are of great importance.

**References**

[1] A. Krzykawska, J. Ossowski, T. Żaba and P. Cyganik, *Chem Comm* **2017** accepted

5:40pm **AS+2D+NS+SA-WeA11 2-D and 3-D Characterization of Functionalized Nanostructured Carbons**, ***Chilan Ngo***, *D.R. Diercks, M.B. Strand, M.J. Dzara, J. Hagen, S. Pylypenko*, Colorado School of Mines

Low cost, versatility, and a broad range of properties make carbon a widely studied material with numerous practical applications. Functionalization/doping with heteroatoms is an effective method to tailor the composition and structure of carbon, in order to adjust its properties for various applications. Significant efforts have been dedicated to elucidation of the composition, structure and properties of doped carbon materials, however atomic scale visualization of high-surface area carbons in 3-D has not been achieved. Here, by utilizing a combination of techniques, we focus on understanding the 2-D and 3-D distribution of nitrogen and iron dopants in high-surface area carbons. Information on surface composition evaluated using X-ray photoelectron spectroscopy (XPS) is complemented by 2-D bulk measurements using energy dispersive X-ray spectroscopy (EDS) through transmission electron microscopy (TEM). 3-D distribution of dopants is studied using atom probe tomography (APT), providing novel insight into the properties of high-surface area carbon materials. This type of investigation necessitated the fabrication of a diverse set of materials with defined shape and morphology, along with variation in the distribution of nitrogen and iron species relative to each other. Nitrogen-doped carbon nanospheres (NCs) were prepared by hydrothermal treatment of resorcinol, formaldehyde, and ethylenediamine, followed by pyrolyzation under flowing nitrogen, producing materials with different dopant concentrations and varied relative distribution of nitrogen functionalities. Iron- and nitrogen-doped nanospheres (FeNCs) were prepared by two routes. For the first set of materials, addition of an iron-containing precursor to the NC synthesis was done prior to hydrothermal treatment, to incorporate Fe throughout the bulk of the nanosphere. The second set is expected to deposit iron only on the surface of the carbon, and is prepared by addition of the iron precursor after the NC pyrolysis, followed by a second pyrolysis. A dual-beam focused-ion beam scanning electron microscope (FIB/SEM) was used to isolate nanospheres into a workable APT tip. Combination of 2-D and 3-D analysis are expected to further the understanding of N-doped carbon materials and N-containing Pt-group metal free catalysts employed in a variety of important catalytic reactions. This work also serves as a foundation to prepare model high-surface area materials that are compatible with *in situ* liquid and electrochemistry TEM techniques, to allow further investigations of these catalytically active materials under conditions relevant to their applications.

6:00pm **AS+2D+NS+SA-WeA12 Characterization of Natural Photonic Crystals in Glitterwing (*Chalcopteryx rutilans*) Dragonfly Wings using 3D TOF-SIMS**, ***Ashley Ellsworth***, *D.M. Carr, G.L. Fisher*, Physical Electronics, *W.W. Valeriano, R.R. de Andrade, J.P. Vasco, E.R. da Silva, A.B.M. Machado, P.S.S. Guimarães, W.N. Rodrigues*, Universidade Federal de Minas Gerais, Brazil

The male Amazonian glitterwing (*Chalcopteryx rutilans*) dragonfly has transparent anterior wings and brightly colored iridescent posterior wings. The colors are important for dragonflies with regard to sexual recognition, mating, and territorial behavior. The source of the varying colors was determined by Valeriano [1] using electron microscopy and optical reflectance to analyze the internal microstructures. SEM and TEM images revealed that the iridescent wings have multiple alternating layers with different electronic densities. The variation of the local color was related to the number and thickness of the layers which varied across the wing. The colors span the visible spectrum with red, blue, and yellow/green regions on the wings. The experimental reflectance was calculated and fitted through the transfer matrix method for the structure obtained from the electron microscopy images. Measurement of the thickness and number of layers is readily achievable by electron microscopy, however it is unable to characterize the chemistry of the different layers giving rise to these natural photonic crystals.

TOF-SIMS is a well-established technique for analyzing the elemental and molecular chemistry of surfaces. TOF-SIMS can now be used to probe the 3D structure and chemistry of a wide variety of organic and inorganic materials, both synthetic and naturally occurring, due to the advent of cluster ion beams such as $C_{60}^+$ and large cluster $Ar_n^+$. We will present results of 3D TOF-SIMS analyses for both transparent and colored wings to correlate with the electron microscopy and optical results to further the understanding of these natural photonic crystals.

[1] W.W.Valeriano, Masters dissertation, UFMG, 2016. Retrieved from http://www.fisica.ufmg.br/posgrad/Dissertacoes_Mestrado/decada2010/wescley-valeriano/WescleyWalisonValeriano-diss.pdf.

## Biomaterial Interfaces Division
## Room: 12 - Session BI+AS-WeA

## In Honor of Dave Castner's 65th Birthday: Multitechnique Bio-Surface Characterization II
**Moderators:** Lara Gamble, University of Washington, Daniel Graham, University of Washington

2:20pm **BI+AS-WeA1 Contributions Advancing Surface Technologies: NEXAFS, ESCA, Rhodium (and More)**, ***Buddy D. Ratner***, University of Washington, Seattle **INVITED**

The broad impact that surface science has had on so many technologies is mirrored by the contributions of Professor David Castner to many sub-fields dependent upon surface science. Dave's earliest contributions to the scientific literature were associated with the surface science of rhodium, iron and cobalt catalysts. Papers were published addressing CO hydrogenation, Fischer-Tropsch polymerization and related topics with relevance to energy consumption and chemical production. With Dave's arrival at the University of Washington in 1986, the subjects of his research shifted from catalysis to biomedical surfaces. Dave and I have always shared a common interest (maybe passion). That is, generating quality data and extracting maximum information from that data. We both had extensive experience with early HP5950 electron spectroscopy for chemical analysis (ESCA) instruments. These monochromatized instruments generated exceptionally high resolution spectra for that era, and the instruments had effective charge compensation for insulators. This allowed us to make great strides in highlighting the use of ESCA for bio-relevant surfaces and biological materials. The theme of data quality has persisted into the present with newer ESCA instruments and then SIMS instrumentation. Dave Castner has taken surface analysis into the 21st century with studies on cells, proteins, novel polymer surfaces and nano-materials. This talk will highlight Dave Castner's remarkable contributions to surface science with particular emphasis on his contributions to the evolution of methods available to analyze complex surfaces and morphologies.

3:00pm **BI+AS-WeA3 Characterization of Bio-Molecules with GCIB-SIMS equipped with MS/MS Spectrometer**, ***Jiro Matsuo***, *T. Seki, T. Aoki*, Kyoto University, SENTA, JST, Japan

Secondary ion mass spectrometry (SIMS) is now widely used for chemical analysis of polymers and biological materials that have a rather complicated molecular structure. Various types of primary ion beams and mass spectrometers have been developed and used in an attempt to improve sensitivity, as well as lateral and mass resolution. Large gas cluster ion beams (GCIB) have been commercialized for surface analysis techniques, such as SIMS and XPS. Molecular depth profiling and three-dimensional analysis have been applied on organic devices and biological materials. A large cluster ion beam could overcome the limitation of ion dose, which is the biggest obstacle for obtaining more signals in static SIMS.

To expand the applications of the SIMS technique, we have developed a finely focused large cluster ion beam (~1mm) for the primary ion beam for use in SIMS [1] and combined it with mass spectrometers of the quadrupole time-of-flight mass spectrometry (Q-TOF) type without pulsing primary ions. This mass spectrometer is equipped with MS/MS capability and allows to determine the structure of the secondary ion by using the collision-induced dissociation (CID) technique. This is a new SIMS instrument that helps in the characterization of biomolecules in cells, tissue and medicine. For instance, the detection limit of a drug molecule is improved by using the MS/MS technique, because of a much-reduced background.

In this paper, we demonstrate the capability of SIMS with the MS/MS spectrometer to determine the structure of molecular-related ions and discuss the benefits and drawbacks of this technique.

[1] J. Matsuo, S. Torii, K. Yamauchi, K. Wakamoto, M. Kusakari, S. Nakagawa, M. Fujii, T. Aoki, and T. Seki, *Appl. Phys. Express,* ***7*** (2014), 056602

3:20pm **BI+AS-WeA4 Linking Nanosilver (AgNP) Toxicity to the Physicochemical Properties of the Particles which can Change as a Function of Experimental and Biological Conditions**, ***Donald Baer***, Pacific Northwest National Laboratory, *J.M. Brown*, University of Colorado at Denver, *A. Porter*, Imperial College London, UK, *B.D. Thrall*, Pacific Northwest National Laboratory, *T.D. Tetley*, Imperial College London, UK, *L.S. Van Winkle*, University of California at Davis, *T. Xia*, University of California at Los Angeles

Although colloidal Ag is generally considered safe for humans, use of nanosilver in consumer products has dramatically increased both the amount of Ag exposure and possible exposure pathways. To fill knowledge gaps for nano-Ag safety assessment, the National Institute of Environmental Health Sciences supported a consortium of investigators to examine how physical and chemical characteristics of AgNPs can lead to adverse health outcomes. Here we report a consortium perspective linking physicochemical properties of the particles to Ag biodistribution and toxicity. It is necessary to recognize the dynamic nature of AgNPs. They can change in response to handling and variations in their environment and such changes can influence Ag biodistribution and biological responses. Consortium studies identified the critical relationships among AgNP properties, environmental effects, and the biodistribution and fate of Ag associated with the particles. Three critical regions of interactions were identified: i) effect of exposure medium and biological environment on particle properties and transformations; ii) processes occurring at the cellular surface impacting particle attachment, uptake, accumulation and clearance; and iii) particle fate and transformations within a cell. The nature of AgNPs during biological exposure is influenced by the initial characteristics of the particles including size, structure and the presence of designed or inadvertent coatings. These initial properties are usually altered by exposure to artificial or natural media. These physicochemical properties are often time dependent and such changes, including often ignored effects due to handling or storage, can influence biological outcomes. Ag can be transported into cells as both ions and particles. While ions are known to impact cytotoxicity, AgNPs within cells often have greater toxicity. Intercellular processes are similar to those in extracellular media except that the Ag is located within specific microenvironments within a cell. It appears that intracellular dissolution of Ag is a major cause of toxicity.

4:20pm **BI+AS-WeA7 Protein Imaging from the Subcellular Level to the Single Protein Level**, ***DaeWon Moon***, DGIST, Republic of Korea

Most of biological story tellings are mainly based on proteins and their interactions. Therefore protein imaging and their interaction studies have been the key interest in bio imaging. Most of protein bioimaging have been based on confocal fluorescence microscopy for 2 or 3 proteins. We have developed a new multiplex protein imaging method for TOF-SIMS with metal oxide nanoparticle (MONP) conjugated with proteins up to 9 proteins, in theory, several tens, and a single protein imaging technique based on He Ion Microscopy (HIM)

In SIMS analysis, MONPs provide high secondary ionization yield and amplification of ion yields. We systhesized 9 MONPs working right such as CoO, CdO, Fe3O4, TiO2, PbO, In2O3, SiO2, Al2O3, La2O3. In addition to protein imaging, SIMS intrinsically provides tens of bio-molecular imaging including lipids and metabolites, and metals with a TOF mass analyzer, which makes this new methodology to be an omni-molecular mass spectrometric imaging technique. Sliced and cultured mouse hippocampal tissues were imaged with typical spatial resolution of 2 µm, which can be improved down to 300 nm for 9 neuronal proteins. Proteins chosen to image mouse hippocampal tissues are NeuN for all nuclei, Cav1,3 for neuron cells, Iba1 for microglia cells, GFAP for astrocytes, AMPA receptor, phosphorylated Tau, amyloid beta (Aß) 1-42, amyloid precursor protein, and APOE, which were selected to visualize important proteins as landmarks of Alzheimer Disease (AD). With multiplex proteins imaging, we could estimate the proximity of associated proteins in mouse hippocampal tissues, which changes with aging and AD progression.

Since HIM has a spatial resolution of 0.5 nm, HIM can observe single proteins in theory but in practice, it may be very dfficult to observe a single protein molecule due to the similar secondary electron yields of proteins compared to other proteins or extracellular matrix molecules. We demonstrated that HIM can image each MONP conjugated with proteins from a mouse hippocampal tissue revealing the distribution of single proteins in synapses, neuronal soma, amyloid plaques, and neurofibrillary tangels with their changes along aging and AD.

With the co-development of multiplex protein SIMS imaging and single protein HIM imaging technology, I expect we can improve our understanding on the role of proteins and their interactions in biology, biomaterials, and medicine.

4:40pm **BI+AS-WeA8 Integrating Biological and Surface Chemical Characterisation to Probe Bacterial and Lipid Vessicle Interactions at Surfaces**, ***Sally McArthur***, Swinburne University of Technology and CSIRO, Australia, *M. Abrigo, H. Askew, K.L. Jarvis*, Swinburne University of Technology, Australia

Control and the ability to elicit specific responses from a biological system lies at the heart of most bioengineering. We want to immobilize proteins on biosensors but ask them to behave as they would in the body, stimulate cells to assemble tissues, form new blood vessels and replicate structures in the lab just as well as they can in our bodies. We want methods that prevent bacteria forming biofilms and better still we would like them to stop attaching to surfaces full stop. We have an armada of techniques at our disposal, surface engineering, macro, micro and nanomaterials, drugs and biomolecules, light, electricity and a plethora of analysis tools to give us new insight into how the systems we build behave. But as we increase the complexity of the system, we need to be able to match this with combinations of characterisation techniques that probe both the biological and physicochemical processes occurring at the biointerface.

This talk will explore how we utilise QCM, XPS, ToF-SIMS, florescence imaging and biological assays to investigate the influence of surface chemistry and micro and nanoscale topography on interactions with lipid vesicles and bacteria.

5:00pm **BI+AS-WeA9 A Physical Chemist and a Chemical Engineer Walk into a Bar… Reflections on Surface and Interface Analysis**, ***Matthew Wagner***, The Procter & Gamble Company **INVITED**

Surface and interface science is critical to many applications across many industries, spanning from advanced technologies in microelectronics and biomaterials to everyday household goods such as laundry detergents and shampoos. Micro and nanoscale phenomena at surfaces and interfaces, including adsorption, wetting, self-assembly, and many others, drive macroscale performance, resulting in significant benefits when done well and significant failures when poorly understood or controlled. At all scales, measurement science specific to surfaces and interfaces is critical to understanding these phenomena.

In the field of biomaterials science (and beyond), protein adsorption is a foundational step in all interactions between biological systems and synthetic materials. Many surface analysis techniques have been applied to the characterization of adsorbed protein films, including understanding the amount, composition, spatial distribution, and orientation of adsorbed proteins. In this special session in honor of Dave Castner, this presentation will review key contributions from the Castner group on the application of multi-technique surface analysis techniques to adsorbed protein films. In particular, the use of ToF-SIMS and multivariate data analysis techniques in conjunction with complementary surface spectroscopies including XPS, NEXAFS, SPR, and others, will be reviewed. The broader impact of these developments in surface analysis methodologies on the fields of surface and interface science across industries will be discussed.

5:40pm **BI+AS-WeA11 Investigating the Cytotoxicity of Commercially Available Poly(*N*-isopropyl Acrylamide)-coated Surfaces**, *L. Stapleton, M.A. Cooperstein, P.A.H. Nguyen,* ***Heather Canavan***, University of New Mexico

Poly (*N*-isopropyl acrylamide) (pNIPAM) is a thermoresponsive polymer that undergoes a phase change at a physiologically relevant temperature range, which leads to mammalian cell release. Below its lower critical solution temperature (LCST ~32° C), pNIPAM becomes hydrated and is hydrophilic. In this state, its chains become extended and cells detach as intact cell sheets. Before the detached cell sheets can be used on humans, the cytotoxicity of the surfaces must be accessed. In previous studies, we found that although most techniques for polymerizing NIPAM (e.g., plasma polymerization, ppNIPAM; and sol-gel preparations of NIPAM, spNIPAM) yielded biocompatible films, those from commercially available NIPAM (cpNIPAM) were relatively cytotoxic. In this work, we investigate the reasons behind this anomaly. The cpNIPAM-coated surfaces were evaluated for their thermoresponse and surface chemistry using standard surface science techniques (e.g., goniometry, X-ray photoelectron spectroscopy). The relative biocompatibility of the substrates with cultured bovine aortic endothelial cells (BAECs) and monkey kidney epithelial cells exposed to extracts from the cpNIPAM, spNIPAM, and ppNIPAM films was assessed using pop off experiments and Live/Dead assays. In addition, the extract solutions themselves were analyzed by NMR and mass spectroscopy. We find that the diminished cell viability of BAECs exposed to cpNIPAM substrates is due to a combination of factors, including the inclusion of short chain length polymers and the presence of unreacted catalyst. This work will have valuable insights into the cytotoxicity of cpNIPAM-coated surfaces, and therefore, into the applicability of cells grown on this surface for human subjects.

6:00pm **BI+AS-WeA12 Development of Surface Analysis Methods for Characterizing Immobilized Proteins**, ***David Castner***, University of Washington

One of the first events that occurs when a biomedical device is placed in the biological environment is the interactions of proteins with the surface region of the biomedical device. How the proteins interact with the surface can have a significant impact on further biological responses in both *in vivo* and *in vitro* applications. Thus, it is essential to understand how proteins interact with surfaces and any structural modifications they undergo as a result of these interactions. Key objectives for characterizing surface-bound proteins are (1) identifying the type of proteins bound to the surface, (2) determining the amount of each surface-bound protein, (3) determining the conformation and orientation of the bound proteins and (4) characterizing the spatial distributions of surface-bound proteins. There are many bonding mechanisms for attaching proteins to surfaces (charge-charge, coordination complexes, covalent bond formation, ligand interactions, etc.). Each method has its advantages and disadvantages. How the protein structure, especially its conformation and orientation, is affected by surface attachment will be a function of the surface structure and composition of the biomaterial as well as properties of the protein. There are often time-dependent changes in the composition, conformation, orientation, and distribution of the complex, multi-component protein films deposited from the biological environment. So the structural determinations for surface bound proteins need to be related not only to the properties of the biomaterial surface and protein, but also to the experimental conditions used to attach the protein to the surface. Results using experimental methods (XPS, ToF-SIMS, SFG, SPR, QCM-D, etc.) combined with computation methods (e.g., MD simulations) provide important information about the attachment, specificity, orientation, conformation and spatial distribution of surface immobilized proteins. This talk will discuss the significant progress has been made in developing surface analysis methods for characterizing the structure of surface immobilized proteins as well as the current challenges. Future protein characterization studies need to be extended to more complex samples as well as more tightly integrating complementary techniques that can be used to directly study immobilized proteins in the presence of the biological environment. In addition, further advances in computational methods for predicting protein-surface interactions and structures as well as providing structural information at the atomic level for large biomolecules is needed.

## 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.

[1] Rycerz et al., Nat. Phys. **3** (2007),172.

[2] Xiao et al., Phys. Rev. Lett. **99**, (2007), 236809.

[3] Wu et al., Phys. Rev. B **84**, (2011), 195463; *ibid* B **86** (2012), 165411; *ibid* B **88** (2013), 125422; *ibid* B **94** (2016), 075407.

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].

[1] D.D. Awschalom, L.C. Bassett, A.S. Dzurak, E.L. Hu and J.R. Petta, Science 339, 1174 (2013).

[2] C. G. Yale, F. J. Heremans, B. B. Zhou, et al., Nature Photonics 10, 184 (2016); B. B. Zhou et al., Nature Physics 13, 330 (2017).

[3] D. J. Christle, A. L. Falk, P. Andrich, P. V. Klimov, et al., Nature Materials 14, 160 (2015); D. J. Christle et al., arXiv:1702.07330 (2017).

[4] A. L. Falk, P. V. Klimov, et al., Physical Review Letters 114, 247603 (2015).

[5] P. V. Klimov, A. L. Falk, D. J. Christle, V. V. Dobrovitski, and D. D. Awschalom, Science Advances 1, e1501015 (2015).

[6] W. F. Koehl et al., Editors Suggestion, Phys. Rev. B 95, 035207 (2017).

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 kΩ 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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[2] M. Kasu, Japanese Journal of Applied Physics 56, 01AA01 (2017).

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.

## Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
## Room: 24 - Session HC+SA+SS-WeA

### Bridging Gaps in Heterogeneously-Catalyzed Reactions
**Moderator:** Yu Lei, University of Alabama in Huntsville

2:20pm **HC+SA+SS-WeA1 Oxygen Reduction Reaction Activity for Pt/Co/Pt(111) and Pt/Co-N/Pt(111) Model Catalyst Surfaces Fabricated by Arc-plasma Depositions**, *S. Kaneko*, *R. Myochi*, *S. Takahashi*, *N. Todoroki*, ***Toshimasa Wadayama***, Graduate School of Environmental Studies, Tohoku University, Japan, *T. Tanabe*, Graduate School of Engineering, Tohoku University, Japan

Comprehensive understanding of oxygen reduction reaction (ORR) activity enhancement mechanisms for Pt-based alloy (Pt-M) catalysts is a key for developing highly-efficient, low-Pt-loading cathode catalysts for polymer electrolyte fuel cell. To clarify the effects of the alloy surface structures (e.g., Pt shell atomic arrangements, Pt/M ratio etc.,) on activity and durability, a number of studies have been performed. We have, thus, investigated ORR properties for the well-defined Pt-based bimetallic single crystal surface alloys prepared by vacuum depositions of metals on single crystal substrates in ultra-high vacuum (UHV) [1]. In this study, ORR activities are investigated for Pt/Co and Pt/Co-N model catalysts prepared on Pt(111) substrate by alternative arc-plasma depositions (APDs) of Pt and Co (Co-N).

The UHV-APD-EC apparatus is described elsewhere [2]. Pt and Co (Co-N) layers were alternately deposited onto a clean Pt(111) substrate by the APDs at 573K in UHV. As for the preparations of Co-N layers, Co was deposited by APD under 0.1 Pa of $N_2$. Total thickness of the Pt/Co(Co-N) and thickness of the topmost-surface Pt and bottom Co layers are fixed to be 6 nm, 1.6nm, and 0.4nm, respectively; the $Pt_{1.6nm}/Co_{0.4nm}/Pt_{3.6nm}/Co_{0.4nm}/Pt(111)$ (denoted as U_Co_4A), U_Co_8A, U_Co_16A, and U_Co_32A samples are prepared. Structural analysis is performed by in-plane XRD, cross-sectional TEM. Then, the Pt/Co/Pt(111) and Pt/Co-N/Pt(111) samples were transferred to an $N_2$-purged glove box without air exposure. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were conducted in $N_2$-purged and $O_2$-saturated 0.1M $HClO_4$ in the glove-box. To discuss EC stability, square-wave potential cycling between 0.6(3s) ~ 1.0(3s) V vs. RHE was applied.

ORR properties (initial activity & durability) of the samples closely correlate with the Co (Co-N) thickness underlying the topmost Pt layer. For example, the activity enhancement factor for the U_Co_16A is highest (13-fold vs. Pt(111)) for the Pt/Co/Pt(111). ORR activity enhancement well corresponds to in-plane lattice distance estimated by the XRD. The results suggest that the ORR enhancements are determined by compressive surface strains that work on the topmost Pt(111) layers induced by underlying Co (Co-N) layers.

We wish to acknowledge the NEDO and JSPS.

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2:40pm **HC+SA+SS-WeA2 The Mechanism of Oxygen Induced p(2×3) Reconstruction on Mo(112)**, ***Teng Ma***, Shenyang Agricultural University, PR China

Oxygen induced reconstruction and oxidation of Mo(112) surface has shown various surface structures in model catalysis and surface studies. Because of its complexity, the p(2 × 3) reconstruction has been modeled as several patterns and its formation mechnism was not well clarified. In this report, a critical precursor of forming p(2 ×3) reconstruction has been observed by using STM, XPS and HREELS methods. For the Mo(112) surface exposed to $5.0\times10^{-8}$ mbar $O_2$, the formation of the p(2×3) reconstruction is a process of two consecutive steps, during which the clean metallic surface experience the initial oxidation to form dispersed oxide particles at nanoscale, and then reduction and structural rearrangement of molybdenum oxides to the ordered nanostructures. The features of surface structures are also temperature dependent, a mixture of dispersed nanoparticles of molybdenum oxide and one-dimensional nanostructures occurs after $O_2$ dose at 605 K, while two-dimensional nanostructures or the p(2×3) reconstruction occurs until above 710 K. Our results would give a good explanation about some hurdled questions about the appearance of LEED streaky points and antidomain dislocations in the STM images of the p(2× 3) reconstruction.

3:00pm **HC+SA+SS-WeA3 Gas-Liquid Scattering Studies of Atmospheric Reactions at the Surfaces of Sea-Spray Mimics**, *M.A. Shaloski, J.R. Gord*, University of Wisconsin - Madison, *S. Staudt*, University of Wisconsin-Madison, *S.L. Quinn, T.H. Bertram*, University of Wisconsin - Madison, ***Gilbert Nathanson***, University of Wisconsin-Madison **INVITED**

Heterogeneous reactions between atmospheric gases and sea-spray aerosols are fascinating examples of complex interfacial processes involving water, ions, and surface-active molecules. These reactions are also important because of the controlling role they play in regulating pollution and greenhouse gases in the troposphere. Of particular interest is the atmospheric molecule $N_2O_5$, created indirectly by fossil fuel burning. During the day, $N_2O_5$ is photolyzed to $NO_2$ and $NO_3$, ultimately producing $O_3$ and then OH· radicals that destroy $CH_4$. During the night, $N_2O_5$ can be removed by dissolving into sea-spray aerosols near coastal regions. This dissolution is followed by rapid hydrolysis to $HNO_3$ or reaction with $Cl^-$ to produce $ClNO_2$, a gas that potentially supplies reactive Cl atoms and returns half of the $NO_2$ to the atmosphere. The fate of $N_2O_5$ upon collision with an aerosol droplet is enormously difficult to predict because the droplets are chemically diverse and often possess an outer layer of lipid-like organic molecules. Such surface-active species can inhibit or even enhance uptake and reactivity by orders of magnitude.

We have implemented gas–liquid scattering experiments to investigate the dynamics of these interfacial $N_2O_5$ reactions. By directing a well-defined beam of $N_2O_5$ at a stream of salty water emerging from a liquid microjet in vacuum, we can track the uptake and reactivity of $N_2O_5$ with seawater and sea-spray mimics. We have also used similar experiments involving liquid glycerol to explore the ability of cationic and zwitterionic surfactants to increase ion concentrations of $Br^-$ or $Cl^-$ at the surface and to stabilize reaction intermediates created by $N_2O_5$. These studies provide insight into interfacial ionization and bimolecular reactions at the surfaces of complex liquids found in the atmosphere.

4:20pm **HC+SA+SS-WeA7 In-situ Investigation of Methane Activation on $MO_x/CeO_2$ (111) Surfaces {M=Co, Ni and Cu} using Ambient-Pressure XPS**, *J. Rodriguez*, ***Zongyuan Liu***, Brookhaven National Laboratory

Natural gas has transformed the energy landscape of this nation and has fast become a cheap and abundant fuel stock. Methane is the primary component of natural gas but is difficult to convert it to upgraded fuels or chemicals due to the strong C-H bond in methane (104 kcal/mol). This challenge constitutes one of the most difficult problems in heterogeneous catalysis. We have discovered a catalyst with small Ni nanoparticles supported on ceria that has shown promising activity for both methane activation and dry reforming of methane. Then we expanded the study to other transition metals (Co and Cu) supported on ceria in order to rationalize the structure-reactivity relationships for methane activation. Due to the chemically inert nature of methane, the experiment needs to be conducted at elevated pressure via the utilization of Ambient Pressure of XPS. Nanoparticles or clusters of Co and Cu were deposited onto the well-defined $CeO_2(111)$ surface. Strong metal-oxide interactions were found upon annealing the deposited surfaces to 700 K, leading to the generation of $MO_x$. In-situ AP-XPS showed that the $CoO_x/CeO_2(111)$ interacted strongly with 50 mTorr of methane, resulting in the formation of $Co/CeO_x(111)$, while no obvious changes were observed on the $CuO_x/CeO_2(111)$ surface (figure 1). By comparing it with the $NiO_x/CeO_2(111)$ surface, it can be found that the methane activation on these $MO_x/CeO_2$ (111) surfaces follow the order: Co > Ni > Cu. The methane dry reforming activity was also investigated on the $CoO_x/CeO_2(111)$ surface by sequentially adding another 50 mTorr of $CO_2$ into the system. The slight reoxidation of the ceria surface indicates the participation of $CO_2$ in the catalytic cycle by the following steps: $CH_4(g) \rightarrow CH_{4-x}(a) + H(a)$ with x=1-4; $CO_2(g) \rightarrow CO(a) + O(a)$; $C(a) + O(a) \rightarrow CO(g)$; $H(a) + H(a) \rightarrow H_2(g)$.

4:40pm **HC+SA+SS-WeA8 Ambient Pressure XPS Study of Catalytic Conversion of Carbon Dioxide by $CuO_x$ Nanoparticles Photodeposited on $TiO_2$ Nanoparticles**, ***Djawhar Ferrah***, *R.P. Galhenage, J.P. Bruce, A.D. Babore, J.C. Hemminger*, University California, Irvine

The chemical conversion of carbon dioxide to useful products has attracted great interest both from a scientific and industrial perspective. It is widely known that Cu is active for the catalytic hydrogenation of $CO_2$. However, the detailed structure and oxidation state of the active site is not well understood. Recently, Cu nanostructures were reported to be a promising catalyst for hydrogenation of $CO_2$ . The main challenge in the development of Cu based transition - metal nanoparticles is thereby bring selectivity and efficiency to heterogeneous catalysis. Due to the wide range of accessible oxidation states ($Cu^0$, $Cu^I$, $Cu^{II}$, and $Cu^{III}$), $CuO_x$-nanoparticules can promote and undergo a variety of reactions which enable reactivity via both one- and two-electron pathways. The size and shape of the particles can play an important role in reactant adsorption and activation at defects and dangling bonds.

In this study, we investigated the reaction mechanisms in carbon dioxide conversion with $CuO_x$ nanoparticles synthesized through the photodeposition process on $TiO_2$ nanoparticles supported on HOPG. We utilize ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to monitor the surface chemistry during in-situ catalytic reaction of $CO_2$ and $H_2$ ($H_2O$) on the surface under ambient pressure conditions. To track the structural and morphological evolution of catalytic nanoparticles, SEM and TEM investigation will be reported.

This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, as follows: The specific development of CuOx nanoparticles on TiO2 nanoparticles was supported through the Office of Science of the U.S. Department of Energy under Award No. DE-SC0004993; The ambient pressure XPS experiments were carried out at the CSX2 end station at NSLS-II. RG is supported by funding from the Provost Office of the University of California, Irvine.

5:00pm **HC+SA+SS-WeA9 Atomic-Scale Characterization of Pt/Ag Surface Alloys**, ***Dipna Patel***, *E.C.H. Sykes*, Tufts University

Catalytic hydrogenation reactions are important in many industrial applications. While Pt is catalytically active towards hydrogenation, it is very costly, can suffer from poisoning by CO, and coke. On the other hand, bulk Ag is catalytically inert towards hydrogenation reactions, but cheaper than Pt and more resilient to poisoning. Previously, Ag based catalysts have been modified for applications in highly selective heterogeneous catalysis. By analogy to our single-atom alloy approach in other systems such as Pt/Cu and Pd/Cu, alloying Pt into Ag has the potential to greatly enhance catalytic selectivity while reducing the cost of precious metal required to catalyze industrially relevant reactions and reduce poisoning. The atomic-scale surface structure of dilute Pt-Ag alloys has not been reported to date. Using scanning tunneling microscopy (STM) and STM-based spectroscopies, we characterized the surface structure and local geometry of low coverage Pt deposited on Ag(111) as a function of temperature. At low temperatures, intermixing of Pt-Ag is driven by a negative mixing enthalpy, resulting in different metastable states such as isolated Pt atoms in, and islands on, Ag terraces, as well as Pt rich brims located along Ag step edges. Increasing the alloying temperature results in an increased concentration of Pt atoms along Ag steps edges as well as direct exchange of Pt atoms into Ag terraces. At higher temperatures, there is sufficient thermal energy for Pt atoms to fully disperse in the Ag(111) surface layer as isolated atoms, forming single-atom alloys. This characterization of Pt-Ag surface alloys will enable us to correlate reaction activity and selectivity to the atomic-scale structure of the alloy and potentially tune catalytic selectivity and resilience to poisoning via both ligand and ensemble effects.

5:20pm **HC+SA+SS-WeA10 Structural Consequences of High Oxygen Coverages on Rh(111)**, ***Rachael Farber****, *M.E. Turano, D.R. Killelea,* Loyola University Chicago

Partial oxidations of small molecules over metal surfaces are central to many heterogeneously catalyzed reactions. However, the identity of the actual surface species that promote or hinder these reactions has remained elusive for a variety of reasons. Recently, the understanding of the role of surface oxides in catalytic activity has changed. Instead of being thought of as poisons, they are now believed to be effective promoters of selective catalysis.

We have chosen to study oxidation on Rh(111) as a model system; Rh effectively promotes oxidation reactions and is a benchmark system for models of heterogeneously catalyzed chemistry. Our approach is to first elucidate the uptake of oxygen on Rh(111) and the surface structures formed for a range of oxygen coverages and then characterize them with a variety of techniques under ultra-high vacuum conditions. Exposure to $O_2$ yields coverages up to 0.5 monolayers (ML), and higher coverages, well in excess of 1 ML, were achieved by dosing with gas-phase atomic oxygen (AO). The surface oxygen coverage was determined with Auger electron spectroscopy (AES), the total oxygen abundance with temperature programmed desorption (TPD), and the surface structures with low energy electron diffraction (LEED) and scanning tunneling microscopy (STM).

Careful control of the exposure parameters allowed for the selective growth of the $RhO_2$ surface oxide, surface adsorbed oxygen, and subsurface oxygen. The combination of AES, TPD, LEED, and STM revealed that despite total oxygen coverages in excess of 3 ML, the surface oxygen coverage was less than 1 ML and the thermodynamically favored surface phase was the (2x1)-O adlayer corresponding to a surface oxygen coverage of 0.5 ML. The $RhO_2$ surface oxide was observed to form during extended oxygen exposures, but the (2x1) adlayer persisted. Our findings highlight the complexity of the surface chemistry of oxygen on transition metals and reveal the consequences of incorporating oxygen into the near-surface region of the solid. Furthermore, formation of the surface oxide was shown to rely not only on the presence of defects, but also on high concentrations of oxygen absorbed below the surface of the metal.

5:40pm **HC+SA+SS-WeA11 Reactivity and Electronic Properties of Supported Metal Oxide and Sulfide Clusters**, ***Michael White,*** Brookhaven National Laboratory, *X. Meng, K. Goodman,* Stonybrook University, *P. Liu,* Brookhaven National Laboratory **INVITED**

Small clusters exhibit electronic and chemical properties that can differ significantly from that of the bulk and offer a unique opportunity for preparing novel catalysts whose reactivity can be modified at the atomic level. Here, we use mass-selected cluster deposition to prepare model "inverse" catalysts comprised of small metal oxide ($M_xO_y$: M = Ti, Nb, Mo, Ce, W) and sulfide ($M_xS_y$: M = Mo, W) clusters deposited on Cu, $Cu_2O$/Cu and Au surfaces for studies the water-gas-shift reaction (WGSR) and for CO/$CO_2$ activation. A key advantage of cluster deposition is that it allows control over cluster stoichiometry which provides a means of introducing oxygen/sulfur "vacancies" and varying the average cation oxidation state. Recent work has focused on the correlation of electron transfer at the cluster-support interface and activity for water dissociation, the latter being a key step in the WGSR mechanism. Electron transfer is probed by XPS core level spectra and 2PPE photoemission measurements of coverage-dependent work function shifts to extract surface dipoles. All the oxide clusters on Cu(111) exhibit negative surface dipoles, indicative of Cu to cluster charge transfer, with smaller dipoles for sub-stoichiometric and reducible oxides (Ti, Nb). Temperature programmed reaction (TPR) experiments show that the $Ti_xO_y$ and $Nb_xO_y$ clusters promote water dissociation on Cu(111), with the 'reduced' $Ti_xO_y$ clusters being more active, while both stoichiometric and reduced $Nb_xO_y$ clusters are active. Overall, these results suggest that local cation coordination is most important for determining water activity. Recent ambient pressure XPS (CO+$H_2O$, 100's mTorr) measurements at NSLS-II show that small $Ti_nO_{2n}$ (n = 3, 4, 5) clusters on Cu(111) are active for the WGSR reaction through the observation of reaction-induced O-vacancy formation ($Ti^{3+}$ 2p) and the appearance of formate intermediates (C 1s) at room temperature. Results will also be presented on investigations of $CO_2$ activation on alkali modified surfaces of $Mo_6S_8$ clusters on Au(111), which had been previously predicted to be active for $CO_2$ hydrogenation to methanol. Combined TPR and XPS measurements show that co-deposition of K-atoms and $Mo_6S_8$ clusters strongly enhances $CO_2$ adsorption above room temperature, whereas the $CO_2$ is only weakly bound on the bare clusters. The results will be compared with DFT calculations of the possible $CO_2$ binding sites for the K-cluster-Au interfaces.

This work was performed at Brookhaven National Laboratory under Contract No. DE-SC0012704 with the U.S DOE, Office of Science, and supported by its Division of Chemical Sciences, Geosciences, and Biosciences.

## Advanced Ion Microscopy Focus Topic
## Room: 7 & 8 - Session HI-WeA

## Emerging Ion Sources and Optics
**Moderator:** John A. Notte, Carl Zeiss Microscopy, LLC

2:20pm **HI-WeA1 COLDFIB – The New FIB Source from Laser Cooled Atoms**, *E. Verzeroli,* ***Anne Delobbe****, M. Viteau,* Orsay Physics, France, *D. Comparat,* CNRS Lac Orsay, France, *A. Houel, M. Reveillard,* Orsay Physics, France **INVITED**

Charged particle beams of controlled energy and strong focusing are widely used tools in industry and science. Focused Ion Beam (FIB) column combine with a Scanning Electron Microscope (SEM) provide full control of nanofabrication or nanolithography processes. Ion energy can be varied typically in the 1–30KeV range, with an energy-dependent resolution attaining the nanometer range. State-of-the-art FIBs commercially available are based mainly on plasma, liquid metal tip or helium ion sources for large, intermediate, and low currents, respectively. Despite the very high technological level of the available machines, research of new ion sources allowing even higher resolution and a wider choice of atomic or molecular ions for new and demanding application is very active.

As an example, the world of electronic components evolves regularly towards the miniaturization by integrating a number of transistors more and more important. The dimensions being smaller and smaller (technology 10 nm, 7 nm even 5 nm), nowadays the instruments of analysis used, like the conventional FIB, reach their limit. Thus it's necessary to realize a technological breakthrough to be able to observe, analyze and modify components and structures on the scale of the nanometer.

Our new system, COLDFIB, wants to take up this challenge of the nanomanufacturing by the coupling of two high technologies: the laser cooling of atoms, and manipulation of charged particles.

Very innovative, this industrial solution, based on a source of ions obtained from atoms laser cooled and ionized, will allow realizing ions beam in the unequalled performances, to reach engraving's sizes of some nanometers. This new technology offers a resolution, for example at 5KeV, 10 times better than the LMIS one, and reaches the nanometer at 30keV *(Figure 1)*.

We'll present in this talk the integration on the SEM-FIB TESCAN instrument. In addition to the experimental[1] part and performances[2] will also show some first applications.

[1] L. Kime, et al., *High-flux monochromatic ion and electron beams based on laser-cooled atoms,* Phys. Rev. A 88, 033424 (2013)

[2] M. Viteau, et al., *Ion microscopy based on laser-cooled cesium atoms,* Ultramicroscopy (2016)

3:00pm **HI-WeA3 FIB Platform Employing a Low-Temperature Ion Source**, ***Adam Steele****, A. Schwarzkopf,* zeroK NanoTech, *J.J. McClelland,* National Institute of Standards and Technology, *B. Knuffman,* zeroK NanoTech

We present a demonstration of a new high-performance ion source retrofitted to a commercial FIB platform. Spot sizes as small as (2.1 ± 0.2) nm (one

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* **Morton S. Traum Award Finalist**

standard deviation) are observed with a 10 keV, 1.0 pA beam. Brightness values as high as $(2.4 \pm 0.1) \times 10^7$ A m$^{-2}$ sr$^{-1}$ eV$^{-1}$ are observed near 8 pA [1]. The measured peak brightness is over 24 times higher than the highest brightness observed in a Ga liquid metal ion source (LMIS); the spot size obtained by operating our source at 10keV is significantly smaller than the spot size achievable with the replaced LMIS operating at 40 keV.

The FIB platform utilizes a Low Temperature Ion Source (LoTIS). As previously described [2], this source is composed of a several discrete stages that collect, compress, cool and finally photoionize a cesium atomic beam. High brightness and small spot sizes are achieved owing to the extremely low (10 uK) temperatures that may be achieved in the neutral atomic beam prior to photoionization. The atomic beam transmits over $5\times10^{10}$ atoms s$^{-1}$, which would be equivalent to an ion beam with over 8 nA if ionized completely; extraction of currents up to 5 nA have been demonstrated to date.

We will present a description of the Cs$^+$ LoTIS-FIB system, together with an examination of the brightness and spot size measurement methodology at beam currents up to a nanoampere. Images acquired using the system will also be shown. Finally, we will describe outcomes of some preliminary milling, gas assisted etching and deposition experiments performed with the system.

[1] A. V. Steele, A. Schwarzkopf, J. J. McClelland, and B. Knuffman. *Nano Futures*. **1**, 015XXX (2017). (to be published 5/2017)

[2] B. Knuffman, A. V. Steele, and J. J. McClelland. *J. Appl. Phys*. **114**, 044303 (2013).

3:20pm **HI-WeA4 Focused Cs Ion Beam Nanomachining and Material Interaction Characterization for Semiconductor Applications**, ***Richard Livengood***, *R. Hallstein, S. Tan,* Intel Corporation, USA, *Y. Greenzweig, Y. Drezner, A. Raveh,* Intel Corporation, Israel, *A.V. Steele, B. Knuffman, A. Schwarzkopf,* zeroK NanoTech, USA

Focused ion beam Nanomachining is used extensively in semiconductor materials and circuit analysis applications. Applications range from using ion beams for large area machining for de-process sample for metrology and defect analysis, to high precision nanomachining to access device circuits [1,2]. There have been many different focused ion beam technologies developed and refined over the last 30 years to perform this type of machining. The two primary focused beam-source technologies used today are: Gallium Liquid Metal Ion source (LMIS) for micro and nanomachining applications [3,4]; and 2) Xenon plasma-cusp ion sources used for bulk material micro-machining in packages interconnects, TSV's, and backend metal layers [5,6]. More recently, the neon and nitrogen (N2) gas field ion sources (GFIS) have also been introduced to enable very small, high precession Nanomachining for circuit rewiring and mask defect repairs respectively [7,8]. Another emerging ion beam / source technology are cold beams (base on ionization of atoms cooled to sub kelvin temperatures, which gives them very low energy spread) [9]. Two such emerging sources are cesium based cold beam sources under development by ZeroK Nanotech Inc. and TOH (Tescan Orsay-Physics Holdings) [10,11].

As part of Intel's due diligence to identify break through ion beam technologies to keep pace with semiconductor scaling requirements and help identify novel analytical applications, Intel has recently been analyzing the attributes of cesium for semiconductor applications [12]. In this paper, we will discuss the attribute requirements for various semiconductor applications and publish early cesium beam machining performance attributes - based on joint characterization experiments performed by Intel and ZeroK Nanotech on cesium LoTIS focused ion beam using ZeroK's proof of concept test platform. Analysis will include preliminary characterization results for material sputter rates, beam induced etching, and other Nanomachining attributes.

4:20pm **HI-WeA7 Spectroscopy in the Focused Ion Beam**, ***Robert Hull***, Rensselaer Polytechnic Institute, *H. Parvaneh*, Global Foundries **INVITED**

We review spectroscopic methods in the focused ion beam (FIB), and introduce the coupled Auger Electron Spectroscopy (AES) – FIB technique. While FIB tomography has become a widely-used method for exploring 3D structure of materials over length scales ranging from tens of nm to tens of µm, complementary high resolution and high sensitivity spectroscopic methods are lacking. Secondary ion mass spectroscopy (SIMS) methods are limited by low ionization yields using conventional Ga$^+$ liquid metal ion source (LMIS) species and/or by low detector transmission factors. The anticipated advantage of coupling AES to the FIB is that Auger electron yields per incident ion can be in the few percent range depending on the experimental conditions, improving on Ga$^+$ ionization yields by several orders of magnitude for many elements. We have integrated an Orsay Physics Cobra mass-selecting FIB column into a PHI VersaProbe X-Ray Photoelectron Spectroscopy (XPS) system, successfully aligning the focal points of the FIB and of the detector/analyzer optics with the necessary precision in 3D dimensions. Using primary ions with different masses (e.g. from an Au-Si alloy source), we can control the relative proportions of the Auger transitions from the atoms of the target sample rather than from backscattered/implanted atoms from the primary beam. We have studied a set of elemental targets, with strong Auger peaks observed from each. For some elements (e.g. Mg, Al and Si), additional extremely sharp peaks are observed, superimposed on the standard Auger peaks. These are due to Auger emission from atoms that have been sputtered from the surface before the inner shell vacancy is filled. The occurrence of these free atom peaks in a subset of the samples can be understood in terms of the substantially longer vacancy state lifetimes in the core levels of some elements, allowing the target atom to escape from the surface field before Auger decay happens. For example, we observe average Auger yields of 0.06 for Cr and 0.09 for Al per incident 60 keV $Si_2^+$ ion. Coupled with the estimated transmission factors and solid angular detection range of the XPS hemispherical analyser employed, this translates into detection of atomic concentrations of order 0.1-1.0 % within a (50 nm)$^3$ voxel. These figures of merit will be compared (favorably) to other spectroscopic methods available in the FIB.

5:00pm **HI-WeA9 Spark-discharge Coupled Laser Multicharged Ion Implantation and Deposition System**, ***Md Haider Shaim***, *M. Rahman, O. Balki, H.E. Elsayed-Ali*, Old Dominion University

Multicharged ions are generated by a Nd:YAG laser ($\lambda$ = 1064 nm, $\tau$ = 7 ns, pulse energy ≤175 mJ ) ablation of aluminum and boron targets in an ultrahigh vacuum. Time-of-flight and electrostatic retarding field ion energy analyzers are used to detect the laser-generated ions. Spark discharge coupling to the laser ion source enhances ion generation along with generating higher charge states than observed with the laser source alone. The spark discharge electrodes are located in front of the target and is triggered by the laser plasma. For an Al target with the laser source alone, the total ion charge delivered to a Faraday cup located 1.4 m away from the source is 1.0 nC with charge state up to Al$^{3+}$. When the spark amplification stage is used (0.1 $\mu$F capacitor charged to 5.0 kV), the total charge increases by a factor of ~9 with up to Al$^{6+}$ observed. The spark discharge increases the multicharged ion generation without increasing target ablation, which solely results from the laser pulse. An electrostatic cylindrical ion deflector is used for analysis and selection of charges with a specific energy-to-charge ratio. A three-electrode cylindrical einzel lens is used to focus the ion beam. A minimum ion beam diameter of ~1.5 mm was obtained. A high-voltage pulse applied to a set of two parallel deflecting plates is used for the pickup of ions with different charge states according to their time-of-flight. Fully stripped B ions with 150 eV per charge are obtained with the laser alone. These ions are used for shallow implantation without further acceleration. Al multicharged ion generation from femtosecond laser ($\lambda$ = 800 nm, $\tau$ = 100 fs, pulse energy ≤1 mJ ) ablation is also studied. Production of Al ions up to Al$^{6+}$ is observed with the laser alone. Compared to nanosecond laser ablation, multicharged ion generation by femtosecond laser ablation require significantly lower laser fluence and generates higher charge states and more energetic ions.

## Manufacturing Science and Technology Group
## Room: 5 & 6 - Session MS+AS-WeA

## Advanced Surface, Interface, and Structural Characterization for High Volume Manufacturing

**Moderator:** Alain C. Diebold, Colleges of Nanoscale Science and Engineering, SUNY Polytechnic Institute

2:20pm **MS+AS-WeA1 The Cornell High Energy Synchrotron Source Upgrade: Current and Future Capabilities for Thin-film Research**, ***Arthur Woll***, Cornell University **INVITED**

In early 2019, the Cornell High Energy Synchrotron Source (CHESS) will complete its most significant upgrade since its construction in 1980. CHESS was originally constructed as a dual-purpose machine, serving as both an x-ray source as well as a particle physics experiment. Since 2008, CHESS has operated as one of only five dedicated high energy synchrotron sources in the world, and one of only two in the U.S.. The upgrade will result in a dramatically improved source, will include six new undulator-fed experimental stations, and represents a unique opportunity to increase and improve access to hard x-ray synchrotron light.

CHESS's history and mission emphasize the importance of deep collaboration with user communities to identify critical areas of instrumentation and methodological development. In particular CHESS has a long history of serving and advancing research on thin films and interfaces – in areas spanning both basic and applied research. CHESS currently hosts active user communities engaged in many of the most promising areas of thin-film research – including organic electronic thin films, high-K dielectrics and other complex oxides, dichalcogenides, and III-V nitrides. Particular research tools include ex-situ characterization such as grazing incidence small- and wide-angle scattering (GISAXS and GIWAXS), fast pole-figure analysis, automated x-ray reflectivity. Specialized equipment for in-situ measurements include chambers for in-situ thermal annealing and solvent annealing, and support for user-supplied UHV chambers for studying in situ thin-film growth and surface science. We will present several examples of recent user science as well as ongoing and proposed CHESS-based developments for thin-film research to motivate a discussion among the thin-film community of the most promising and critical areas for future capabilities of CHESS.

3:00pm **MS+AS-WeA3 Using Synchrotron XRD Techniques to Impact Microelectronics Manufacturing Technologies**, ***Jean Jordan-Sweet***, *C. Lavoie*, IBM T.J. Watson Research Center, *A.V. Carr*, IBM Research, Albany, NY, *N. Breil*, IBM SRDC, East Fishkill; now with Applied Materials Inc., *M.M. Frank*, IBM T.J. Watson Research Center **INVITED**

Since the early 1980s IBM has maintained a strong effort in synchrotron-based research. While our involvement with these facilities has been multi-faceted, we have leveraged our impact through two main avenues: the development of unique instrumentation and the nurturing of mutually beneficial collaborations with academia.

I will present examples of how synchrotron-based XRD studies have impacted our heavily materials- and process-centric technologies, preceded by a description of the instrumentation and techniques that were developed and applied in these examples. Much of our success in supporting IBM technology has been based on the use of *in-situ* XRD, electrical resistance, and optical light scattering measurements during the rapid thermal annealing of thin films or arrays of features. This instrumentation was developed at the NSLS (Brookhaven National Laboratory) [1], and has been redesigned, automated and recently installed at the Canadian Light Source. A second technique that is crucial for understanding the microstructure of thin polycrystalline films on single-crystal substrates is the measurement of texture. With the use of a linear or area detector, many high-resolution pole figures covering a large range of d-spacing can be obtained simultaneously [2]. Understanding and controlling film texture is critical to controlling phase transformations in thin films and to stabilizing and enhancing thermal processing windows during device manufacturing [3].

The first example is a long-term effort to understand the effects of materials and processing on the formation of low-resistance contacts to the gate, source and drain of CMOS devices. It has spanned three materials sets and many generations of chips. The culmination of this knowledge lies in a valuable database containing structure, roughness and resistance information from many thousands of anneals on key samples. With these measurements, IBM was able to extend the manufacturing lifetime of C54-$TiSi_2$, stabilize the NiSi process, and recently resolve a Ni “fang” defect [4] related to the IBM Power8® processor. The second example illustrates how the same techniques are helping us develop advanced memory devices based on ferroelectric hafnium oxide, which are intended to be used for neuromorphic computing.

1] G.B. Stephenson et al., Rev. Sci. Instrum. 60, 1537, 1989; L.A. Clevenger et al., J. Mater. Res. 10, 2355 (1995); J.L. Jordan-Sweet, IBM J. Res. Develop. 44, 457 (2000).

2] S. Gaudet et al., J. Vac. Sci. Technol. A 31(2), 021505 (2013).

3] B. DeSchutter et al., Appl. Phys. Rev. 3, 031302, 2016; C. Lavoie et al., ECS Transactions (accepted).

4] N. Breil et al., Microelectron. Eng. 137, 79 (2015).

4:20pm **MS+AS-WeA7 Development of Ultra-thin ALD Grown high-k Dielectrics and Interconnect Diffusion Barrier Layers aided by Advanced X-ray Structural Analysis for sub 10nm Nodes**, ***Steven Consiglio***, *K. Tapily, R.D. Clark, C.S. Wajda, K.-H. Yu, T. Hakamata, G.J. Leusink*, TEL Technology Center, America, LLC, *S. Dey, A.C. Diebold*, Colleges of Nanoscale Science and Engineering, SUNY Polytechnic Institute **INVITED**

As the semiconductor industry develops processes and integration schemes for the 10nm technology node and beyond, conventional scaling of existing materials is no longer sufficient to enable further device scaling. New materials in the form of ultra-thin films need to be introduced and evaluated at an ever-increasing pace and conventional inline wafer metrology systems do not offer the needed flexibility and capabilities to probe the physical/chemical/structural properties of such extremely scaled layers of increasing complexity.

In this regard, we have investigated the properties of ultra-thin high-k dielectrics and interconnect (both Cu and Ru) diffusion barriers using advanced synchrotron X-ray structural analysis. Some key examples will be illustrated including analysis of higher-k phase stabilization and texturing in thin dielectrics on Si and high mobility substrates, ferroelectric phase stabilization for negative differential capacitance dielectrics, and the evaluation of diffusion barrier performance by using an in-situ ramp anneal method for both Cu and Ru which is a potential Cu interconnect replacement metal.

References:

S. Consiglio et al., *J. Electrochem. Soc.*, **159**(6), G80-G88 (2012).

K. Tapily et al., *ECS Trans.*, **45**(3), 411-420 (2012).

R. Vasić et al., *J. Appl. Phys.*, **113**, 234101 (2013).

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K. Tapily et al., *ECS J. Solid State Sci. Technol.*, **4**(2), N1-N5 (2015).

S. Consiglio et al., *ECS J. Solid State Sci. Technol.*, **5**(9), P509-P513 ( 2016).

S. Dey et al., *J. Appl. Phys.*, **120**, 125304 (2016).

S. Dey et al., *J. Vac. Sci. Technol. A*, **35**(3), 03E109 (2017).

5:00pm **MS+AS-WeA9 Stress Control of rf Sputter Deposition of Piezoelectric $Sc_{0.12}Al_{0.88}N$**, ***Michael Henry***, *R.P. Timon, T.R. Young, E.A. Douglas, B. Griffin*, Sandia National Laboratories

Substitution of Al by Sc has been predicted and demonstrated to improve the piezoelectric response with applications in radio frequency (RF) filter technologies. Although cosputtering has achieved Sc incorporation in excess of 20%, industrial processes require single target sputtering and is currently limited. However, the major concern with sputter deposition of ScAl is the control over growth of inclusions while simultaneously controlling film stress for suspended MEMS structures. Our work on 12% Sc suggests, with a direct relationship between the inclusion occurrences and compressive film stress, deposition control can suppress the inclusion growth by increasing the compressive stress. Too much compressive stress can prevent suspension of MEMS devices due to Euler buckling.

This work will describe the RF sputtering deposition and major parameter control over the deposition of $Sc_{0.12}Al_{0.88}N$. We will continue to show a multistep deposition which begins with a process of high compressive stress suppressing the inclusions and then drive the film back towards lower compressive stress levels such that an inclusion free low compressive stress film is deposited such that suspended resonators can be formed. To detail piezoelectric film properties, both top metal and top/bottom metal resonators are demonstrated from 500 MHz to 2 GHz.

## Nanometer-scale Science and Technology Division
## Room: 19 - Session NS+MN+MS+SS-WeA

## Nanopatterning, Nanofabrication and 3D Nanomanufacturing
### Moderator: Brian Borovsky, St. Olaf College

2:20pm **NS+MN+MS+SS-WeA1 Site-controlled Si Nanodot Formation for a RT-SET via Ion Beam Mixing and Phase Separation**, ***Xiaomo Xu****, *G. Hlawacek, D. Wolf, T. Prüfer, R. Hübner, L. Bischoff*, Helmholtz Zentrum Dresden-Rossendorf, Germany, *M. Perego*, Institute for Microelectronics and Microsystems (IMM-CNR), France, *A. Gharbi*, Laboratoire d'électronique des technologies de l'information (CEA-Leti), France, *H.-J. Engelmann, S. Facsko, K.-H. Heinig, J. von Borany*, Helmholtz Zentrum Dresden-Rossendorf, Germany

The increased use of personal computing devices and the Internet of Things (IoT) is accompanied by a demand for a computation unit with extra low energy dissipation. The Single Electron Transistor (SET), which uses a Coulomb island to manipulate the movement of single electrons, is a candidate device for future low-power electronics. However, so far its development is hindered by low-temperature requirements and the absence of CMOS compatibility. By combining advanced top-down lithography with bottom-up self-assembly of Si nano dots (NDs) we will overcome this barrier.

In this work, Si NDs – suitable as RT Coulomb islands – are formed via ion beam mixing followed by thermally stimulated phase separation. Broad-beam $Si^+$ and $Ne^+$ beams followed by a rapid thermal annealing (RTA) treatment were utilized to create a layer of NDs, which are subsequently visualized by Energy-Filtered Transmission Electron Microscopy (EFTEM). The conditions for ND formation, namely the dependence on ion type, primary energy, irradiation fluence, layer thickness and thermal budget during RTA, are optimized based on an extensive survey of this multidimensional parameter space. The presented work is guided by TRIDYN simulations of the Si excess in a $SiO_2$ layer due to ion beam mixing

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* **NSTD Student Award Finalist**

and 3D Kinetic Monte-Carlo (3DkMC) simulation for the phase separation during the thermal treatment. To tailor towards a single Si ND, the focused Ne+ beam from the Helium Ion Microscope (HIM) is utilized to create user defined patterns of NDs in planar layer stacks. This allows to achieve a mixing volume small enough for restricted Ostwald ripening and successful single ND formation. The existence of the formation of spatially controlled single NDs with a diameter of only 2.2 nm is confirmed by comparing the EFTEM Si plasmon-loss intensity with simulated plasmon loss images.

In the future – by combining conventional lithography, direct self-assembly (DSA) and ion beam mixing – nanopillars with a single embedded ND will be integrated in a CMOS-compatible way. EFTEM and electrical characterization techniques will be used for realizing this novel pathway towards a room-temperature SET device.

2:40pm **NS+MN+MS+SS-WeA2 Scanning Tunneling Microscope Fabrication of Atomically Precise Devices**, ***Richard Silver***, NIST, *X. Wang*, University of Maryland, College Park, *P. Namboodiri, J. Wyrick, S.W. Schmucker, M.D. Stewart, R. Murray, J.A. Hagmann, C. Richter*, NIST

Atomically precise device fabrication is a technique that enables a new class of atom-based electronic structures with applications ranging from novel low dimensional materials to devices for quantum information processing. Deterministic placement of individual dopant atoms in the Si lattice is achieved using hydrogen-based scanning probe lithography. Controlling the position and electronic or quantum state of deterministically placed atoms in a solid state environment enables novel devices such as single atom transistors and solid state qubits.

However, fabricating functional atom-based devices is particularly challenging because of the need for exceptional ultra-high vacuum, near perfect atomic order, and low temperature epitaxial silicon overgrowth. This, coupled with sensitivity of atomic positional accuracy to thermal processing, and variability in scanning tunneling microscope patterning conditions, make exquisite control of process conditions essential.

In this presentation, we will focus on measurements and characterization of ultra-thin, atomically abrupt, highly doped low-dimensional devices and strategies for contacting these devices. We will describe our methods to align and contact buried devices and address significant challenges in making robust electrical contact to buried devices. We will present low-temperature electrical measurement results from atomically abrupt wires and tunnel junctions with coplanar gates. We have studied the effects of process conditions on device dimensionality and electrical performance in the context of extensive analysis of delta layer formation with optimized locking layer epitaxial growth techniques to enhance the confinement of Phosphorus dopant atoms. Low temperature transport measurements are used to investigate materials properties, effects from atomic imperfection and quantum transport phenomena.

3:00pm **NS+MN+MS+SS-WeA3 Contacting Buried Atomic-Precision Devices in Si using Kelvin Probe and Optical Microscopy**, ***Jonathan Wyrick***, *P. Namboodiri, X. Wang, R. Murray, J.A. Hagmann, K. Li, S.W. Schmucker, M.D. Stewart, C. Richter, R.M. Silver*, NIST

STM based hydrogen lithography has proven to be a viable route to fabrication of atomic-precision planar electronic devices. These devices are realized by a patterning step followed by dopant deposition and incorporation, and ultimately encapsulation with epitaxial Si. Atomically precise tunnel junctions, SETs, and Quantum Dots are examples of components that can be fabricated using hydrogen lithography.

The strength of this technique is the ability to control the lateral placement of phosphorus atoms in a single atomic layer of Si with sub-nanometer precision. At the same time, it presents challenges that must be overcome if devices are to be interfaced to the outside world. Locating and then fabricating aligned electrical contacts to buried devices is non-trivial, and becomes easier as the size of buried features is increased, but this is done at the expense of increased writing times and exposure to potential contamination.

We present a strategy for contacting buried devices aimed at minimizing the write-times associated with STM based fabrication by maximizing the positional accuracy with which we can locate subsurface structures. This is done by employing STM fabricated fiducials, AFM topography scans, Kelvin Probe Microscopy, and dark field optical microscopy. The data from each technique can be aligned and corrected for distortions, allowing us to determine buried device locations to better than 200nm accuracy.

3:20pm **NS+MN+MS+SS-WeA4 Quantifying Liquid Transport and Patterning using Atomic Force Microscopy**, *N. Farmakidis*, ***Keith Brown***, Boston University

Atomic force microscopy (AFM) provides unique insight into the nanoscale properties of materials. It has been challenging, however, to use AFM to study soft materials such as liquids or gels because of their tendency to flow in response to stress. Here, we propose an AFM-based technique for quantitatively analyzing the transport of soft materials from an AFM probe to a surface. Specifically, we present a method for loading an AFM probe with a single 0.3 to 30 pL droplet of liquid, and subsequently measuring the mass of this liquid by observing the change in the vibrational resonance frequency of the cantilever. Using this approach, the mass of this liquid was detected with pg-scale precision using a commercial AFM system. Additionally, sub-fL droplets of liquid were transferred from the probe to a surface with agreement found between the real-time change in mass of the liquid-loaded probe and the volume of the feature written on the surface. To demonstrate the utility of this approach in studying nanoscale capillary and transport phenomena, we experimentally determine that the quantity of liquid transported from the tip to a surface in a given patterning operation scales as the mass of liquid on the probe to the 1.35 power. In addition to providing new avenues for studying the dynamics of soft materials on the nanoscale, this method can improve nanopatterning of soft materials by providing *in situ* feedback.

4:20pm **NS+MN+MS+SS-WeA7 Positioning and Manipulating Single Dopant Atoms Inside Silicon**, ***Andrew Lupini***, *B.M. Hudak, J. Song*, Oak Ridge National Laboratory, *H.R. Sims*, Vanderbilt University, *M.C. Troparevsky*, Oak Ridge National Laboratory, *S.T. Pantelides*, Vanderbilt University, *P.C. Snijders*, Oak Ridge National Laboratory **INVITED**

The ability to controllably position single atoms inside materials could enable production of a new generation of atomically precise artificial materials with direct relevance for many areas of technology. For example, spins from individual donors in a semiconductor comprise one of the most promising architectures for quantum computing. However, fabrication of the ‘qubits’ that would make up a quantum computer is still unreliable and many fundamental materials science questions remain unanswered. Perhaps the key technical difficulty is the task of accurately positioning single atom dopants inside a solid with control, or at least understanding, of their local environment.

Silicon is the ideal substrate to explore such ideas because of the ability to obtain isotopically purified samples (a “spin-vacuum”) and compatibility with existing electronic components and manufacturing technologies. Group V elements are promising candidates for use as single-atom qubit dopants in Si, and it has recently been argued that bismuth could be an excellent dopant for such applications, because of its anomalously high spin-orbit coupling. Bi, in particular, has a large atomic number relative to Si, making it an ideal candidate to study using *Z*-contrast scanning transmission electron microscope (STEM). However, both precise doping and the imaging of single dopant atoms present many scientific challenges. For example, Bi is not very soluble in Si, meaning that the dopant atoms tend to migrate out of position during sample growth.

Here we will show examples of sample growth including novel nanostructures and single atom dopants. We will show dopant atoms imaged inside Si samples, and demonstrate electron-beam directed movement of single dopants.

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5:00pm **NS+MN+MS+SS-WeA9 Characterization of Butyl Tin Photoresists for Nanoscale Patterning**, *J.T. Diulus, R.T. Frederick*, Oregon State University, *M. Li*, Rutgers University, *D. Hutchison, M.R. Olsen, I. Lyubinetsky, L. Árnadóttir*, Oregon State University, *E.L. Garfunkel*, Rutgers University, *M. Nyman*, Oregon State University, *H. Ogasawara*, SLAC National Accelerator Laboratory, ***Gregory Herman***, Oregon State University

Inorganic photoresists are of interest for nanomanufacturing due the potential for high resolution patterning with low line edge roughness, while having high sensitivity to extreme ultraviolet (EUV) radiation. The combination of high absorption coefficient elements and radiation sensitive ligands can improve inorganic photoresist sensitivity while providing high contrast. Inorganic clusters are ideal candidates for photoresists since they have nanometer particle sizes with high particle size uniformity, and the ligand chemistries can be tuned for radiation induced chemistries that control relative solubility differences. In this presentation, characterization of a promising inorganic cluster-based EUV photoresist will be presented, where the goal of the studies is to better understand patterning mechanisms. In these studies, we are investigating butyl tin Keggin cluster that has recently been synthesized, and has shown promising properties as an inorganic photoresist. Key to these clusters, for application as an EUV photoresist, are the high EUV absorption coefficient for Sn, and the radiation sensitive carbon-tin bond. Removal of the organic ligand changes the polarity of the film, which provides the necessary solubility contrast for nanopatterning. We have used temperature programed desorption, electron stimulated desorption, and ambient pressure X-ray photoelectron spectroscopy to characterize both thermal and radiation induced processes in thin films formed from these clusters. We have found that butyl group desorption occurs through both thermal and radiation induced processes, and have determined both the carbon-tin bond strength and electron desorption cross-sections. Studies performed in different ambient conditions, and photon energies, have shown large effects on the radiation induced chemistries, where a significant enhancement in carbon decay was observed for $O_2$ pressures up to 1 torr. These studies provide a means to better understand the radiation induced processes that result in the solubility contrast of these materials, and may guide in the development of improved EUV photoresists for nanolithography.

5:20pm **NS+MN+MS+SS-WeA10 Impact of Polymer Templated Annealing on Gold Nanowires**, ***Tyler Westover***, *R.F. Davis, B. Uptrey, J. Harb, A. Woolley, S. Noyce*, Brigham Young University

The formation of gold nanowires using bottom up nanofabrication has resulted in wires of small dimension or high conductivity, but not both. We form nanowires on DNA origami through directed assembly of nanoparticles or nanorods followed by electrochemical plating. These metal deposition processes result in non-ideal microstructure and correspondingly low conductivities. To remedy this we have sought to reduce the grain boundary density and surface roughness through annealing. However annealing causes the wires to coalesce into beads. We have found that through the use of a polymer the wires can be templated to retain their overall morphology, while improving surface roughness, throughout a low temperature anneal. We have measured these wires to have less than 1kOhm resistances by electron beam lithography, in a two point configuration. Using electron beam induced deposition we have successfully made four point contacts to measure the change in resistance due to annealing. We will present results on polymer templating, showing that the wires maintain their overall morphology with improved conductivities during low temp (200° C) annealing.

5:40pm **NS+MN+MS+SS-WeA11 Dynamic Growth of Nanopores on Graphene via Helium Ion Microscope**, *S. Kim*, ***Anton Ievlev***, *M.J. Burch, I. Vlassiouk, A. Belianinov, S.V. Kalinin, S. Jesse, O.S. Ovchinnikova*, Oak Ridge National Laboratory

Controlling atomic-to-nanoscale defect formation on graphene is of significance as defects can modify properties as well as functionality of graphene. Especially, controlled formation of nanopores in graphene can be used for energy harvesting/storage, analysis of biomolecules and the separation of gases or liquids. Nanopores can be fabricated either by using high energy focused electron beam or by focused helium ion beam with high precision. However, focused electron beam has very low throughput to form nanopores despite its superiority in pore size control. On the contrary, focused helium ion beam has much higher throughput in nanofabrication with its capability to form sub-5nm pores. In this study, we utilized the focused helium ion microscope to fabricate nanopores on graphene and demonstrated atomic scale control in growth of nanopores by helium ion irradiation. We demonstrated the size control of nanopores down to ~ 3nm in a diameter. Formation and growth kinetics of nanopores by different helium ion irradiation conditions were explored and analyzed using the image data analytics. Also, Raman spectroscopic measurements was performed to demonstrate the effect of a helium ion dose on the change of initial defect density on graphene which leads to different behaviors and growth kinetics of nanopore formation.

This work was supported by the Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy, Office of Science User Facility.

## Plasma Science and Technology Division
## Room: 22 - Session PS+SS+TF-WeA

## Plasma Deposition
**Moderators:** Jeffrey Shearer, IBM Research Division, Albany, NY, Thorsten Lill, Lam Research Corporation

2:20pm **PS+SS+TF-WeA1 Correlation Between Ion Energies in CCRF Discharges and Film Characteristics of Titanium Oxides Fabricated via Plasma Enhanced Atomic Layer Deposition**, ***Shinya Iwashita***, *T. Moriya, T. Kikuchi, N. Noro, T. Hasegawa*, Tokyo Electron Limited, Japan, *A. Uedono*, University of Tsukuba, Japan

A plasma enhanced atomic layer deposition (PEALD) process for synthesizing titanium oxide ($TiO_2$) thin films, which allows to modify the film properties by tuning the ion energies of capacitively coupled radio frequency (CCRF) discharges, was performed. $TiO_2$ films were deposited via the oxidation of titanium tetrachloride using a typical CCRF discharge in argon/oxygen mixtures, and the energy distributions of ions hitting an electrode (wafer surface) during the deposition were adjusted by controlling the impedance of the electrode [1]. The wet etching rate of $TiO_2$ films shows a clear correlation with the mean ion energy; a higher mean ion energy realizes a higher value of the wet etching rate. The film characteristics are varied due to the balance between the oxidation and ion bombardment during the PEALD process. In a high mean energy condition, fine pores are formed in films due to the bombardment of high energetic ions, which was confirmed by the physical analyses such as positron annihilation spectroscopy. One can conclude that the energy control of ions in CCRF discharges is interpreted as tuning the oxidation and ion bombardment, both of which determine the film characteristics.

[1] K. Denpoh et al Proc.38th Int. Symp. Dry Process, 183 (2016).

2:40pm **PS+SS+TF-WeA2 Functionalized Titanium-Nitride Surfaces Formed by Femtosecond-Laser Processing**, ***David Ruzic***, *S. Hammouti, B.J. Holybee*, University of Illinois at Urbana-Champaign, *B.E. Jurczyk*, Starfire Industries

Thin films surfaces are playing an increasing role in the application of smart materials. This covers the improvement of surface properties like hardness, corrosion resistance, thermal, magnetic properties and so on depending on the application field. Many methods evolved for the preparation of thin films and coatings and among them the laser surface treatment. Since a decade, femtosecond laser micro-machining has been successfully introduced in industry for optic, surface wetting, biological or catalytic applications. The high precision achieved with femtosecond lasers for drilling or texturing purposes originates primarily from the limited heat affected zone which is greatly reduced compared to that of laser systems with longer pulse duration such as nano or picosecond. Moreover, ultrafast laser surface processing provides a simple way of nanostructuring and surface functionalization towards optical, mechanical or chemical properties. Indeed, irradiation of surfaces with short laser pulses of high intensity in a reactive atmosphere can result in a direct coating formation if the laser parameters are properly adjusted.

In this study, femtosecond laser processing of titanium surface in nitrogen (laser nitriding) has been investigated due to technological importance of nitrogen in metals and alloys for fusion applications. A two-step process consisting firstly to a femtosecond laser texturing of titanium surface under argon and then under nitrogen, both at atmospheric pressure, has been used. The laser treatment under argon has been proved to be efficient to remove most of the oxide layer which otherwise reduce the formation of titanium nitride. Several laser parameters for both laser treatments have been tested to obtain the best combination for the generation of titanium nitride. Beside chemical modifications of titanium surface, the formation of self-organized micro/nanostructures usually observed after irradiation in an ultrashort regime which result in topographic modifications are also of the high interest for wetting properties. Due to nonthermal effects involved in the ultrashort femtosecond processes the normal nitrogen diffusion process, as in the case of nanosecond laser nitriding. The titanium nitride layer produced by the femtosecond pulses most probably corresponds to nitride fall out from the recondensing plasma formed after the laser pulse above the irradiated surface, containing titanium and nitrogen ions and atoms.

3:00pm **PS+SS+TF-WeA3 Controlling the Thin Film Properties of Silica Synthesised by Atmospheric Pressure-Plasma Enhanced CVD**, ***Fiona Elam****, A.S. Meshkova,* FOM institute DIFFER, Netherlands, *B.C.A.M. van der Velden-Schuermans, S.A. Starostin,* FUJIFILM Manufacturing Europe B.V., *M.C.M. van de Sanden, H.W. de Vries,* FOM Institute DIFFER, Netherlands

Atmospheric pressure-plasma enhanced chemical vapour deposition (AP-PECVD) is an innovative technology that can be integrated into many existing manufacturing systems to facilitate the mass production of functional films; specifically encapsulation foils. These barrier films are essential to the flexible electronics industry, envisioned to protect devices such as flexible solar cells and organic light emitting diodes against degradation from oxygen and water.

Industrially and commercially relevant roll-to-roll AP-PECVD has been used to deposit silica thin films onto flexible polyethylene 2,6 naphthalate substrates by means of a glow-like dielectric barrier discharge using an air-like gas mixture. Single and bilayer films were evaluated in terms of their encapsulation performance, their chemical structure, the nature of their porosity and their morphology, with respect to the deposition conditions.

It was found that by increasing the plasma residence time and reducing the precursor (tetraethyl orthosilicate (TEOS)) flux, the specific input energy per TEOS molecule could be enhanced, which in turn resulted in the deposition of films with a lower intrinsic porosity. However, an input E/TEOS greater than 9 keV was found to limit the encapsulating performance of single layer barrier films, due to the creation of ~1 μm diameter pinhole defects. This restriction was overcome by the deposition of a semi-porous silica ‘buffer’ layer between the polymer substrate and silica ‘barrier’ layer. The buffer layer within the bilayer architecture acted as a protective coating to prevent excessive plasma-surface interactions that can occur during the harsh processing conditions necessary to generate dense barrier films. As a result, the bilayer films demonstrated exceptionally low effective water vapour transmission rates in the region of $2\times10^{-4}$ g m$^{-2}$ day$^{-1}$, values so far unprecedented for silica encapsulation barriers deposited at atmospheric pressure on flexible polymer substrates. Finally, regarding process throughput for the manufacture of silica thin films capable of protecting flexible solar cells, a 140% increase in processing speed was achieved for bilayer films with respect to 100 nm single layer barriers of equivalent encapsulation performance.

3:20pm **PS+SS+TF-WeA4 Plasma Information Based Virtual Metrology for Nitride Thickness in Multi-Layer Plasma-Enhanced Chemical Vapor Deposition**, ***Hyun-Joon Roh*****, S. Ryu, Y. Jang, N.-K. Kim, Y. Jin, G.-H. Kim,* Seoul National University, Republic of Korea

Advanced process control (APC) is required to assure the quality and throughput of plasma-assisted process. For this purpose, the process result of all wafers should be measured. However, direct metrology can measure only 1~3 wafers within a lot due to slow time response. To improve the speed of metrology, virtual metrology (VM) is alternatively adopted to support APC. VM can predict the process results close to real-time, since it predicts the process results by using statistical methods based on equipment engineering systems (EES) and sensor variables. However, previously developed VMs face the degradation of prediction accuracy as the chamber wall condition drifts in long-term process. This robustness issue is originated from that the used input variables of VM cannot recognize the drift of chamber wall condition. To enhance the robustness even in a process with severe drift of chamber wall condition, we propose PI-VM that uses plasma information (PI) as input variables of statistical methods. Experimental application of PI-VM is performed to predict the nitride film thickness in multi-layer plasma-enhanced chemical vapor deposition (PECVD) for 3D NAND fabrication which has a severe drift of chamber wall condition. PI variables are composed of the chamber wall condition ($PI_{Wall}$) and property of bulk plasma ($PI_{Plasma}$) considering plasma-surface interaction. Each PI variable is decomposed from $N_2$ emissions in optical emission spectroscopy (OES) by analyzing them based on optics and plasma physics. Then, PI-VM is constructed by implementing PI and EES variables to partial least squares regression (PLSR). Compared to conventional VM, PI-VM improves the robustness more than twice in long-term variation by implementing $PI_{Wall}$ on PLSR. Also, evaluation of the ranking of variables on PI-VM shows that the robustness is improved by decomposing $PI_{Wall}$ and $PI_{Plasma}$ from OES based on optics and plasma physics. This result showed that an effective VM model for plasma-assisted process can be constructed by making phenomenological-based, statistical-tuned VM model that recognizes the drift of chamber wall condition and property of plasma separately, based on optics and plasma physics.

4:20pm **PS+SS+TF-WeA7 Sidewall Effects in the Modulation of Deposition Rate Profiles of a Capacitively Coupled Plasma Reactor**, ***Hojun Kim***, Samsung Electronics Co. Ltd., Republic of Korea **INVITED**

In the recent semiconductor industry, plasma-enhanced chemical vapor deposition (PECVD) using capacitively coupled plasma (CCP) is often chosen to coat a thin uniform film with a high production efficiency. Since inside of a CCP reactor, a discharge volume is radially surrounded by a sidewall, the modulation of the sidewall surface can contribute to controlling distributions of plasma variables. In this study, we thus investigate the sidewall effects by varying the electrical condition of the sidewall from grounded to dielectric. In the cases with the dielectric sidewalls, a cylindrical insulator with a grounded exterior surface is adopted, and then its radial thickness is additionally varied from 2 mm to 45 mm. As an example for the particular case of PECVD, $SiH_4$/He discharge during deposition of an amorphous hydrogenated silicon (a-Si:H) film is simulated using a two-dimensional fluid model. The cases with the thick insulators have more uniform distributions of the plasma variables than the case with the grounded sidewall or the case with the thin insulator. An increase of the showerhead radius also improves a distribution uniformity because non-uniformity sources of the plasma distribution are set further away from the electrode edge.

5:20pm **PS+SS+TF-WeA10 Linear Magnetron Magnetic Field Optimization for HiPIMS Industrialization**, ***Ian Haehnlein****, J. McLain, B. Wu, I. Schelkanov,* University of Illinois at Urbana-Champaign, *B.E. Jurczyk,* Starfire Industries, *D.N. Ruzic,* University of Illinois at Urbana-Champaign

High power impulse magnetron sputtering (HiPIMS) has time and time again been proven to provide superior film qualities over direct current magnetron sputtering (DCMS) due to increased ion fraction at the substrate. Throughput however is decreased due to the increase in return of sputtered target material [1]. Work done previously at the Center for Plasma Material Interactions (CPMI) at the University of Illinois Urbana-Champaign by Raman et al. introduced the Tripack for a 4” circular magnetron. This magnet configuration features three distinct racetracks with magnet fields tuned to allow electron escape from the magnetron magnetic field during high power pulses [2]. This was used in a linear magnetron to increase the deposition rate of HiPIMS. McLain et al. has shown using a 5x11” linear magnetron a decrease in the confinement parameter of during DC from 6 using a conventional magnet pack to 3 using the Tripack designed for a linear magnetron. Deposition rates for HiPIMS using Tripack increased deposition rates over the conventional pack by ~25% for copper. In the 1.5kW case the HiPIMS discharge using the Tripack was ~1nm/s greater than that of DCMS using the conventional magnet pack. Triple Langmuir probe measurements at the substrate verified an increase of several orders of magnitude over the conventional pack, supporting the theory that a decreased electron confinement would increase deposition rate, further supported by an increase in ion-neutral fraction at the substrate from ~12% to 35% measured at the substrate surface. Due to non-uniform redeposition on the target surface the, preferentially towards the center, that the outer racetracks eroded faster and subsequentially had stronger magnetic fields at the target surface. The inner racetrack fails to ignite, causing uneven erosion of the target. It is proposed that by creating a serpentine magnet pack which utilizes the reduced confinement parameter seen in the Tripack with only one racetrack as to confine electrons evenly over the target surface. Deposition rates, electron densities, and ion-neutral fractions for the improved magnet pack are provided in this work. These values are presented with and without the use of a positive polarity modified waveform controlling ion deposition energy independent of the substrate for a better controlled deposition on insulators or temperature sensitive materials.

5:40pm **PS+SS+TF-WeA11 Investigating the Effect of the Substrate at Short Deposition Times for Plasma Polymerised Films**, ***Karyn Jarvis****, N.P. Reynolds,* Swinburne University of Technology, Australia, *L.D. Hyde,* Melbourne Centre for Nanofabrication, Australia, *S.L. McArthur*, Swinburne University of Technology and CSIRO, Australia

Plasma polymerization modifies surfaces via the deposition of a thin film containing specific functional groups. The organic monomer is introduced into the chamber as a vapour, fragmented via radio frequency and deposited onto all surfaces in contact with the plasma. Plasma polymerization is typically referred to as ‘substrate independent’, but is this true for short deposition times? Does the substrate conductivity, chemistry or roughness influence the early stage deposition of plasma polymer films? In this study, plasma polymerized acrylic acid (ppAAc) and allylamine (ppAA) were deposited onto glass, silicon, gold and fluorinated ethylene propylene (FEP) substrates for deposition times of 10 to 600 seconds. Surface chemistry was investigated using X-ray photoelectron spectroscopy while surface roughness was determined using atomic force microscopy. Film thickness

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* **Coburn & Winters Student Award Finalist**

measurements were made by spectroscopic ellipsometry and wettability determined via contact angle measurements. Different contact angle behaviours were observed between the deposition of ppAAc and ppAA films, while different substrates resulted in different contact angle trends for ppAA. For ppAAc films deposited for 10 seconds, all substrates became more hydrophobic (80-100°) and was proposed to be due to 'island' film formation, which would increase surface roughness and therefore increase hydrophobicity. For ppAA films deposited for 10 seconds, the contact angles of all substrates except FEP increase/decrease to 60-70° and do not significantly change as deposition time increase. Such behaviour suggests the ppAA films may deposit continuously from the start, unlike ppAAc which may initially form film islands. Unlike all the other substrates, FEP showed the same behaviour for both monomers, suggesting initial island formation for both monomers. These initial results suggest that for short deposition times, the underlying substrate does have some influence on the formation of plasma polymerized films.

## Plasma Science and Technology Division
## Room: 23 - Session PS-WeA

### Modeling of Plasmas
**Moderators:** Kostya (Ken) Ostrikov, Queensland University of Technology and CSIRO, Richard van de Sanden, DIFFER

2:20pm **PS-WeA1 TSV Etch Plasma Modelling from Chamber to Feature**, ***Sebastian Mohr***, Quantemol LTD, *S. Rahimi, A. Dzarasova*, Quantemol LTD, UK

A key goal of the presented research project PowerBase is to produce new integration schemes which enable the manufacturability of 3D integrated power GaN smart systems with high precision TSV etched features. This project is a collaboration of 39 partners focused on exploring novel materials and manufacturing processes optimisation and testing. Quantemol's contribution to the PowerBase project includes the simulation of the Rapier reactor built by SPTS presented here. This tool allows control of the homogeneity of particle fluxes to the wafer via two independently controlled coils and two independently controlled nozzles. In this project, the Rapier is used to etch through Si wafer via the BOSCH process. By combining simulation and experiment, we look for the parameter settings, which ensure homogeneous etch rates and features with a minimal amount of scalloping. This presentation includes the simulations of the reactor in both $SF_6$ and $C_4F_8$ performed with Q-VT/HPEM as well as feature profile simulations. Due to the complicated chemistries, the non-trivial geometry of the reactor, and limited diagnostics, simulating the Rapier is an arduous task. As this presentation will show, we managed to achieve excellent agreement between experimentally and computationally obtained surface rates. The reactor simulation employs fluid techniques to calculate the particle densities and fluxes as well the electric fields and a Monte Carlo Simulation of the reactive species, both neutrals and ions, to obtain the distribution of these particles at the wafer with regards to both energy and angle (IEADFs). FInally, the IEADFs and particle fluxes are used in the feature profile model, which alternates between the polymer deposition process in $C_4F_8$ and the etching process in $SF_6$ , which in this case is almost exclusively driven by the chemical etch of silicon by fluorine radicals. Due to the isotropic nature of the chemical etch, a certain amount of scalloping is to be expected. The simulation identified the effect of key parameters such as the ICP and rf-bias power on the feature profile, as well as the homogeneity of particle fluxes. These insights were transferred to the experiment with the final goal to achieve the optimal combination of radially homogeneous surface rates, smooth features, and process time. This presentation highlights the challenges of simulating the Rapier, comments on the agreement between simulation and experiment, and analyses the effect of parameter variations such as power and gas flow on the flux homogeneity and feature profile.

2:40pm **PS-WeA2 Global Model based Framework for Prediction of Ion Energy Distributions Under Pulsed RF-bias Conditions in Plasma Etching Processes**, ***Shogo Sakurai***, ET Center, Samsung R&D Institute Japan, *S. Lim,* Samsung Electronics, Korea, *R. Sakuma, S. Nakamura, H. Kubotera, K. Ishikawa,* Samsung R&D Institute Japan, *K. Lee*, Samsung Electronics

Prediction of ion energy distributions (IEDs) under real process condition is one of the critical issues in plasma etching processes of micro-fabrication of semiconductor devices. In this study, we developed global (volume-averaged) model based framework to predict the IEDs under the real conditions with pulsed RF bias, dual/triple frequencies, and the high power sources. By employing global model as the core module, our framework achieves not only strong robustness compared with existing higher dimensional equipment simulators for the severe conditions, but also acceptable simulation time as daily simulator for extensive low pulse frequency such as 100Hz. Furthermore, our framework was applied to wide variety of plasma reactors: inductively coupled plasma, capacitively coupled plasma (CCP), and microwave-excited surface wave plasma, by cooperation with electron heating model corresponding to the reactor type and the radio-frequency (RF) sheath model. On the other hand, the framework requires larger computational cost to obtain the results than original global model of steady state problems. Thus, our effort was much paid to reduce the time by utilizing numerical algorithms such as adaptive time stepper, hybrid time-integrator, etc. Especially, employed RF sheath model was expressed by one-dimensional fluid equation for ionic species which can be solved numerically by Runge-Kutta integration scheme; the integration also demands large computational cost due to the self-consistent coupling to equivalent circuit of RF biased substrates. Therefore, some sort of evaluation way of the model was needed for the reduction. Actually, the sheath model is used to calculate sheath width only on our model for evaluation of the sheath capacity. Fitting function to the numerical solution was employed to evaluate the value quickly. The obtained function has same asymptotic behavior as Child-Langmuir law for high potential drop limit. Furthermore, the curve of the function well reproduces the numerical solution for entire ranges of the potential drop where past analytical formula failed to reproduce. By using the function, we found that the simulation gains the speed by 39.1 times for pulsed dual RF CCP plasma with Argon gas compared to the unused case. The expression of the function was also extended to the numerical solutions of the electronegative plasma such as $Cl_2$ gas to gain the application range.

3:00pm **PS-WeA3 Understanding Particle-Surface Interactions and Their Importance in Plasma Processing: a Plasma Modelling Perspective**, ***Andrew Gibson***, *S. Schroeter, D. O'Connell, T. Gans,* University of York, UK, *M.J. Kushner,* University of Michigan, *J.-P. Booth,* LPP-CNRS, Ecole Polytechnique, France **INVITED**

Low-temperature plasmas are widely used in a number of important applications. Specific examples include the etching of nanoscale structures in the semiconductor industry, electric propulsion of spacecraft, and as reactive species sources in biomedicine. In all of these applications, the plasma is bounded by surfaces and as a result, particle-surface interactions play a crucial role in defining its properties. These interactions act as sources and sinks of charged and neutral particles and enable energy transfer processes that heat and cool the plasma. As such, particle-surface interaction processes can influence all aspects of the plasma dynamics, and a proper understanding of their effects is crucial to optimizing a given application.

However, for a given plasma-surface combination a complete picture describing all possible particle-surface interaction processes is almost never known. This is a major reason why numerical simulations of low-temperature plasmas, where probabilities for various particle-surface interactions are used as boundary conditions, are often challenged to predict the results of experimental investigations. The work presented here seeks to provide insights into several key particle-surface interaction processes occurring in prominent applications of low-temperature plasmas using a combination of zero- and two-dimensional numerical simulations. In particular, the role of atomic neutral species surface recombination, excited species surface quenching, neutral thermal energy accommodation and electron- and ion-induced secondary electron emission probabilities in defining the properties of low-temperature plasmas will be discussed.

Examples of the importance of these particle-surface interactions in both low-pressure plasma sources, used in the semiconductor industry for etching processes, and atmospheric pressure micro-plasmas, used as radical sources in biomedicine, will be presented. It was found that surface processes play a key role in both examples and strongly affect plasma parameters important for applications. In the low-pressure case, this includes the neutral-to-ion flux ratio, a key parameter for precision etching processes. At atmospheric pressure, the densities of radical species and the overall chemical composition of the plasma, key parameters for interactions with biological tissue, are found to be particularly affected. In each example, areas where particle-surface interactions may be harnessed to optimize applications through the tailoring of surface properties will be highlighted.

Funding through the LABEX Plas@Par project, ANR-11-IDEX-0004-02 and UK EPSRC Manufacturing Grant (EP/K018388/1) is acknowledged

4:20pm **PS-WeA7 Investigation of Pulsed $Ar/O_2/CF_4$ Capacitively Coupled Plasmas**, ***Wei Tian***, *S. Rauf, K.S. Collins*, Applied Materials, Inc.

High selectivity has become a critical requirement for many etching processes during microelectronics fabrication. These processes require good uniformity (both etch rate and critical dimensions) in addition to high selectivity. To meet these challenges, pulsed capacitively coupled plasmas (CCPs) have been introduced due to their ability to better control the flux of ions and radicals to the substrate as well as the energy of the ions incident on the substrate. By pulsing the plasma, one can more effectively modulate the electron energy distribution and the electron impact source functions of reactive species compared to traditional methods.[1,2] Pulsing introduces many additional control variables to already complicated etch processes. In addition, a variety of pulsing schemes are possible in multi-frequency CCPs. To optimize the pulsed CCPs processes, understanding of the transients during a given pulse is the key.

In this work, we will investigate the pulsed $Ar/O_2/CF_4$ CCPs using results from a 2-dimensional plasma equipment model.[3] We consider single and dual frequency CCPs, and both single source and synchronous pulsing schemes are investigated. The ignition of the plasma is influenced by the ramp-up of the applied voltage. An overshoot in electron density, electron temperature as well as in emission during the ignition is observed. Depending on the pulse frequency and duty cycle, the plasma during a pulse can be influenced by the previous pulse. The metastable states have a lifetime of milliseconds and are able to accumulate pulse-by-pulse. Through Penning ionization of metastable states, electron and ion densities are affected. The after-glow phase is important for controlling of ion flux and energy, and depends on the voltage decay and sheath collapse. The modeling results are also compared to experimental measurements for validation.[4]

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[2] A. Agarwal, S. Rauf, and K. Collins, J. Appl. Phys. **112**, 033303 (2012).

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### 4:40pm **PS-WeA8 Modeling of Silicon Etching using Bosch Process: Effects of Oxygen Addition on the Plasma and Surface Properties**, ***Guillaume Le Dain***, STMicroelectronics / CNRS-IMN, France, *A. Rhallabi*, Cnrs - Imn, France, *S. Elidrissi*, University of Nantes, *C. Cardinaud, A. Girard*, Cnrs - Imn, France, *F. Roqueta, M. Boufnichel*, STMicroelectronics, France

Bosch process is currently used for semi-conductors devices manufacturing. This technique performs high aspect ratio features by alternating $SF_6$ and $C_4F_8$ plasma pulses. These features are needed for some micrometric scale systems such as Microelectromechanical Systems (MEMS) and System in Package (SiP). One of the problem encountered in silicon etching under Bosch process is the difficulty to minimize the scalloping effect characterized by the propagation of the ripples along the sidewall and to maintain a high etch rate.

Usually, a pure $SF_6$ plasma pulse for etching step and pure $C_4F_8$ plasma pulse for deposition step are used in silicon Bosch process. The aims of our study are to analyze the effect of oxygen addition to both $SF_6$ and $C_4F_8$ plasmas pulse on the silicon etching profile evolution and to understand how the oxygen could improve the etching anisotropy and minimize the scalloping effect. Indeed, previous works reveal that the addition of oxygen to $SF_6$ plasma for silicon etching under cryogenic process contributes to the sidewall passivation of etched silicon and thus to the improvement of the anisotropy [1]. In this context, we have added $O_2$ gas to our $SF_6$ and $C_4F_8$ plasmas module as well as sheath and surface modules of silicon etching simulator. This is to investigate its effect on the silicon etching profile evolution under Bosch process [2]. Our etching simulator is composed of three modules: 0D plasma kinetic module, 2D sheath module and 2D surface module. It allows the prediction of the silicon etching profile evolution as a function of the operating conditions such as power, pressure, flow rate, plasmas pulses times and bias.

The effects of $\%O_2$ on the electrical and kinetic properties of plasmas are analyzed. Moreover, its impact on the silicon etching profile evolution under the mask is presented.

Comparisons between the simulation and the experiments give satisfactory agreements for both plasma discharges and silicon etching profiles.

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### 5:00pm **PS-WeA9 A Mixed Mode Parameter/Physical Driven Particle-in-cell (PIC) Code for Capturing Transient Response and Evolution Behavior of Laboratory Plasma**, ***Noel Lauer***, *N.J. Ianno*, University of Nebraska-Lincoln

A baseline *1d3v* full particle-in-cell (PIC) code has been modified extensively and is described. Modifications include the addition of a *local densityadjustment* (LDA) to the Monte-Carlo-Collision (MCC) algorithm to facilitate the study of plasma transients due to external pulsed stimulus and evolution behavior of plasma in general. The LDA-MCC adjusts for conditions involving transient volume density distributions and population inversions, collisions outside the sputter injected material wavefront, zero population cells, extreme volume density gradients, and collisional vs. colliding species role reversals. Additional modifications were made to accommodate collisional interactions between the working gas neutrals (WG), ions ($WG^+$), and electrons ($e^-$) with cathode target material neutrals ($T_n$) and ions ($T^+$). The MCC was further altered to distinguish WG fast neutrals ($WG_{fn}$) and excited atoms ($WG^*$) to support de-excitation and Penning collisions important in high power impulse magnetron sputtering (HiPIMS). A comparative summary of particle-particle interactions supported vs. the baseline code are shown in Table 1 supplemental. Further changes were made to support parameter, physical, and mixed mode driven simulation regarding secondary emission coefficients (SEEC), target emission coefficients (TAEC), and their underlying implementation at the cathode. A physical driven model to support electron emission $\delta_e$ and a parameter driven target ion sticking coefficient has also been incorporated at the anode. Further revisions were made to accommodate SEECs and TAECs greater than 100% requiring changes to the charge adjustment algorithm. Finally, the particle mover and injection push algorithms were modified to support a decaying magnetic field $B_z$ parallel to and sourced from the cathode.

When new material is introduced via sputter injection or HiPIMS is utilized, new material wavefronts and locally high volume densities can arise, Fig. 1 supplemental, causing incorrect collision statistics if treated as a uniformly distributed density throughout the plasma. Furthermore, large numbers of zero population cells can exist for individual species for periods of time during plasma evolution. These characteristics can produce collision results where source material is non-existent, Figs. 2-3 supplemental, and infer more collisions than existing source material. These discrepancies can be insignificant after the plasma has equilibrated but are unacceptable when studying transient behavior or the details of plasma evolution. The LDA-MCC makes adjustment for these scenarios.

### 5:20pm **PS-WeA10 Investigating Mode Transitions in Pulsed Inductively Coupled Plasmas**, ***Steven Lanham***, *M.J. Kushner*, University of Michigan

Pulsing the power applied to inductively coupled plasma (ICP) systems has beneficial effects, such as lowering average ion energies and customizing the flux of reactive species to surfaces [1]. With pulsed plasmas being increasingly used in semiconductor fabrication, more of the processing time is in a transient regime. For example, in many ICP systems pulsing the power repeatedly transitions between electrostatic (E-mode) power deposition at the start of a power pulse and inductive (H-mode) power deposition later during the power pulse [2]. This transition results from the large variation of the electron density, particularly for electronegative gas mixtures, and plasma impedance during a pulse. For the highly electronegative gases often used for processing, the plasma can essentially extinguish in the afterglow of a pulse and require reigniting at the start of every pulse.

In this paper, we discuss mode transitions for power deposition in pulsed ICP systems based on results from a computational investigation. The Hybrid Plasma Equipment Model (HPEM), a 2-dimensional plasma multi-fluid model [3], was used to simulate the consequences of the E-H transition resulting from capacitive coupling in pulsed ICPs. We found that for highly electronegative gas mixtures, such as $Cl_2$ at a few to tens of mTorr, the power initially applied at the beginning of a pulse is essentially purely capacitive. The dominance of sheath centric power deposition during startup can then launch electrostatic waves into the plasma, an outcome that is sensitive to antenna frequency and pulse repetition frequency. Choosing to operate with a ramped current or ramped power at the onset of a pulse can, in some instances, constrain operation to E-mode or allow a faster transition from E- to H-mode. The pulse power format has a first order effect – controlling current or controlling power – on the E-H transition, and the stability of the plasma.

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This work was supported by the National Science Foundation and the Department of Energy Office of Fusion Energy Science.

5:40pm **PS-WeA11 Science of Plasma-Surface Interaction for Modern Semiconductor Process Technologies**, ***Satoshi Hamaguchi****, *K. Karahashi*, Osaka University, Japan **INVITED**

The fast development and rapidly spreading use of Information and Communication Technologies (ICT) worldwide are firmly founded on the continuing development of semiconductor device technologies. With an increasing demand for higher integration density of large-scale integrated (LSI) circuits with lower energy consumption, device sizes continue to shrink, their structures become more complex (such as those of 3D multigate fin FETs), and unconventional materials (such as magnetic materials for MRAMs) are used for semiconductor devices. Challenges for plasma processing technologies used for LSI device fabrication therefore lie in the development of new plasma chemistry that allows processing with atomic-scale accuracy for existing as well as new materials used for crucial parts of semiconductor devices. Processing with atomic-scale accuracy is required to minimize material damages induced by ion bombardment, which means more chemistry-driven, rather than physical-sputtering driven, processes must be employed. For the development of plasma etching chemistry, the guiding principle is to find volatile molecules that can be formed from materials to be etched. However, unlike silicon or germanium based materials, which can be etched by the formation of volatile halides, most metal or metal oxides do not form volatile molecules under low-pressure plasma conditions. For example, the formation of volatile metal-organic complexes (such as metal carbonyls) from a metal or metal oxide surface is unlikely to occur in a low-pressure plasma as their coordinate covalent bonds are so weak that they could be easily broken by ion bombardment. The authors have analyzed etching chemistries of various materials, such as metal oxides, magnetic metals, amorphous carbon, as well as Si-based materials, using multi-beam experiments [1] and molecular dynamics (MD)/first-principle quantum mechanical (QM) simulations. In this work, we shall summarize our recent work on etching mechanism analyses and attempt to predict the future direction of process development.

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## Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
## Room: 9 - Session SA+AS+HC+SS-WeA

## In Situ and Operando Characterization of Interfacial Reactions in Energy & Electronic Devices

**Moderators:** Karen Chen-Wiegart, Stony Brook University/Brookhaven National Laboratory, Elke Arenholz, Lawrence Berkeley National Laboratory

2:20pm **SA+AS+HC+SS-WeA1 Probing Solid-Gas and Solid-Liquid Interface Using APXPS**, ***Zhi Liu***, *J. Cai, Q. Liu*, ShanghaiTech University, PR China, *Y. Han*, Chinese Academy of Sciences, PR China, *J. Liu*, ShanghaiTech University, PR China, *M. Mao, H. Zhang*, Chinese Academy of Sciences, PR China, *Y. Li*, ShanghaiTech University, PR China **INVITED**

Multiple new ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations are currently under planning or development at US and international synchrotron light sources. Most of the research has been focused on the solid-gas interfaces. [1] Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5keV- 5keV). By using X-ray up to 5KeV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. [2] In this talk, I will present results of in-situ studies on the electrolyte/electrode interface of a working model electrochemical cell. I will also give a brief introduction on the APXPS development in Shanghai.

We believe the successful development of soft and hard X-ray APXPS techniques will provide us and community beyond a powerful in-situ tool to directly study interface phenomena at Solid-Gas and Solid-Liquid Interfaces.

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3:00pm **SA+AS+HC+SS-WeA3 Graphene Capped Static and Fluidic Systems for In-Liquid Atmospheric Pressure XPS/AES/SEM and PEEM Studies of Electrochemical Interfaces**, ***Hongxuan Guo***, *E. Strelcov, A. Yulaev,* NIST, Center for Nanoscale Science and Technology*, S. Nemšák, D.N. Mueller, C.M. Schneider,* Peter Grünberg Institute and Institute for Advanced Simulation, Germany, *A. Kolmakov*, NIST, Center for Nanoscale Science and Technology

The liquid-solid electrochemical interfaces are a central topic of modern energy-related electrochemistry and catalysis research. For the last two decades, this research line benefited greatly from the development of differentially pumped electron optics and refreshable sample delivery systems which became an experimental core of the modern ambient pressure electron spectroscopy. An alternative experimental approach to atmospheric pressure electron microscopy (SEM[1], SPEM[2], PEEM[3]) and spectroscopy (XPS[4-5], XAS[3,6]) has been recently tested. In this approach, high electron transparency and molecular impermeability of the graphene membrane was employed to separate the liquid or gaseous sample from ultra-high vacuum environment of electron spectrometer.

In this presentation, we will show our recent work on design and performance of the static and fluidic microfabricated arrays (MCA) capped with bilayer graphene. With such a liquid cell, we characterized water and aqueous solution employing synchrotron-based and standard laboratory XPS, SEM, EDX, and Auger spectroscopy setups[7]. In particular, Cu electroplating and copper sulfate electrolyte polarization at the graphene working electrode have been studied spectroscopically in real time and nanoscopic spatial resolution.

Acknowledgement

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3:20pm **SA+AS+HC+SS-WeA4 A 3D Printed Liquid Cell for Soft X-ray Absorption Spectroscopy**, ***Tom Regier****, T.D. Boyko, J. Dynes, Z.N. Arthur,* Canadian Light Source, Inc., *M.N. Banis*, University of Western Ontario, Canada

Research methods that enable operando studies on energy materials are an important tool for the rational design of materials for renewable energy and carbon neutral technologies. Of particular value is the ability to observe the change in configuration of the 3d orbitals in transition metal based catalysts. Using the excitation of 2p electrons into vacant 3d orbitals, synchrotron based L-edge measurements allow for clear observation of chemical state and co-ordination geometry information from the first row transition elements. Challenges related to the operating in-situ flow cells in soft x-ray beamline endstations have been overcome and operando measurements are now possible at several facilities.

We report on the design of a 3D printed liquid flow cell with built-in electrodes for operando measurements of the transition metal L-edges. The disposable cells can be quickly customized for specific experiments and can be pre-ordered for lab-based characterization before attempting synchrotron measurements. Beamline instrumentation allows for highly sensitive fluorescence yield measurements with 10 micron spatial resolution or 1 minute time resolution.

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*** PSTD Plasma Prize Winner**

### 4:20pm **SA+AS+HC+SS-WeA7 In Operando Quantification of Valence Changes in Memristive Devices**

*R. Dittmann*, ***Christoph Baeumer***, Peter Gruenberg Institute, Forschungszentrum Juelich GmbH, Juelich, Germany, *D. Cooper,* Université Grenoble Alpes & CEA, LETI, Minatec Campus, Grenoble, France, *C. Schmitz, S. Menzel, C.M. Schneider, R. Waser*, Peter Gruenberg Institute, Forschungszentrum Juelich GmbH, Juelich, Germany **INVITED**

Memristive devices based on resistive switching in transition metal oxides are attractive candidates for next-generation non-volatile memory applications. It is suspected that voltage-driven oxygen-ion migration and the resulting nanoscale redox processes drive the resistance change in these materials[1, 2]. Direct observation and quantification of the switching mechanism itself, however, remain challenging because the net changes of structure, stoichiometry, and valence state during switching are very small and occur primarily at electrode interfaces or within nanoscale filaments.

Here we will present local changes in the chemical and electronic structure of $SrTiO_3$-based memristive devices utilizing *in operando* characterization tools like transmission electron microscopy (TEM) and photoemission electron microscopy (PEEM). $SrTiO_3$ is chosen as a single crystalline model material, which offers a well-understood platform and well-characterized spectroscopic signatures.

To overcome the surface sensitivity typically limiting PEEM investigations of memristive devices, photoelectron-transparent graphene top electrodes are used to attain spectroscopic information from the buried $SrTiO_3$ layer[3]. During *in situ* switching, reversible changes of the O K-edge absorption spectra within spatially confined regions provide a quantitative map of the oxygen vacancy concentration, confirming that the resistance change is caused by localized oxygen evolution and reincorporation reactions rather than purely internal movement of oxygen vacancies[4].

A remarkable agreement between experimental quantification of the redox state and device simulation reveals that changes in oxygen vacancy concentration by a factor of 2 at electrode-oxide interfaces cause a modulation of the effective Schottky barrier and lead to >2 orders of magnitude change in device resistance. These findings allow realistic device simulations, opening a route to less empirical and more predictive design of future memory cells.

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### 5:00pm **SA+AS+HC+SS-WeA9 Magnetic Skyrmions in Ultrathin Magnetic Films and Nanostructures**

***Jan Vogel***, Institut Néel, CNRS/UGA, Grenoble, France, *O. Boulle, R. Juge,* SPINTEC, CNRS/CEA/UGA, Grenoble, France, *D.S. Chaves, S. Pizzini,* Institut Néel, CNRS/UGA, Grenoble, France, *S.G. Je, G. Gaudin,* SPINTEC, CNRS/CEA/UGA, Grenoble, France, *T.O. Mentes, A. Locatelli,* Elettra-Sincrotrone Trieste, Italy, *M.U.J. Foerster, L. Aballe*, ALBA Synchrotron Light Facility, Spain **INVITED**

Magnetic skyrmions are chiral spin structures with a whirling spin configuration. Their topological properties, small size and sensitivity to small current pulses have opened a new paradigm for the manipulation of magnetization at the nanoscale. Chiral skyrmion were first experimentally observed in bulk materials [1] and in epitaxial ultrathin films [2], under a strong external magnetic field or at low temperature. More recently, it was predicted that they can also be created in thin magnetic films in stacks with structural inversion asymmetry [3]. We have used high lateral resolution PhotoEmission Electron Microscopy combined with X-ray Magnetic Circular Dichroism (XMCD-PEEM) to show that skyrmions with a size around 150 nm can indeed be stabilized at room temperature and without external magnetic field, in nanostructures of Pt/Co/MgO with a Co thickness of 1 nm [4]. The high sensitivity of the technique allows measuring very thin Co layers buried under protecting cover layers. The vectorial information obtained by rotating the sample with respect to the incoming x-ray direction allowed us obtaining information on the 3-dimensional spin structure of the skyrmions, directly showing the chiral spin configuration with left-handed chirality.

We investigated the dependence of the skyrmion size on an applied magnetic field, revealing that already a moderate field of 4 mT can reduce the skyrmion diameter to a size of 70 nm. We also studied the motion of skyrmions in micron-wide strips of Pt/Co/MgO induced by current pulses. The results show that skyrmions can be moved with moderate current pulses with current densities of some $10^{11}$ A/m$^2$, leading to velocities of several tens of m/s.

Our measurements show that synchrotron-based magnetic imaging using PEEM is very powerful for studying the static and dynamic properties of skyrmions in ultrathin magnetic films.

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### 5:40pm **SA+AS+HC+SS-WeA11 $O_2$ Pressure Dependence of $SiO_2$/Si Interfacial Oxidation Rate Studied by Real-time Photoelectron Spectroscopy**

***Shuichi Ogawa***, Tohoku University, Japan, *A. Yoshigoe,* JAEA, Japan, *S. Ishidzuka,* National Institute for of Technology, Akita College, Japan, *Y. Takakuwa*, Tohoku University, Japan

Thermal oxidation of Si surfaces under the non-equilibrium conditions were used to form a high-quality Si oxide films and/or enlarge the oxidation rate. For example, rapid thermal oxidation (RTO) is performed under the raising the temperature, and then thick oxide can be formed without preventing the dopant diffusions[1]. In addition, the oxidation rate of RTO process is faster than that of constant temperature oxidation (CTO) though the highest temperature of RTO is as same as that of CTO[2]. Based on these knowledges, it is predicted that the oxidation rate at the $SiO_2$/Si interface can be quickened even by increase of the $O_2$ pressure. In this study, the increased $O_2$ pressure dependence of the interface oxidation rate which proceeds contentiously after Si(001) surface oxidation was investigated using real-tile photoelectron spectroscopy.

The oxidation experiment was performed using the surface reaction analysis apparatus placed at the BL23SU of SPring-8, Japan. A clean Boron doped p-type Si(001)$2\times1$ surfaces were oxidized at 400°C under the $O_2$ pressure of $3.2\times10^{-5}$ Pa. When clean surfaces were completely covered by the Si oxide, the $O_2$ pressure was elevated to $P_{O2}$(int) in order to enhance the interfacial oxidation. The $P_{O2}$(int) was changed between $6.4\times10^{-5}$ Pa to $3.2\times10^{-3}$ Pa. O 1s and Si 2p spectra were measured repeatedly during the oxidation. The time evolution of O 1s photoelectron intensity ($I_{O1s}$) was used for investigation of the oxidation rate.

From the $I_{O1s}$, we can estimate the completion of surface oxidation as 3200 s. An $O_2$ pressure was increased up to $1.5\times10^{-3}$ Pa at this time, and then the interface oxidation was enhanced. The enhanced interfacial oxidation rates were obtained from the differential of $I_{O1s}$. The $P_{O2}$(int) dependence of the interfacial oxidation rate shows that the $O_2$ pressure increase makes the interfacial oxidation rate fast, and the interface oxidation rate is proportional to the square root of $P_{O2}$(int).

This result cannot be explained using traditional oxidation models, because the proportional relationship between the interface oxidation rate and square root of $P_{O2}$(int) indicates that the interface oxidation rate is limited by an $O_2$ diffusion through the oxide. However, the thickness oxide is much thinner than 1 nm, so that it cannot be thought that the rate-limiting reaction of interfacial oxidation is $O_2$ diffusion. To explain the kinetics, we propose the new interface oxidation model named “Unified Si oxidation model mediated by point defects”[3].

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### 6:00pm **SA+AS+HC+SS-WeA12 Highly Time-resolved Insights into the Sputter Deposition of Metal Electrodes on Polymer Thin Films for Organic Electronics**

***Franziska Löhrer***, *V. Körstgens,* Technische Universität München, Germany, *M. Schwartzkopf,* Deutsches Elektronensynchrotron DESY, Germany, *A. Hinz, O. Polonskyi, T. Strunskus, F. Faupel,* Christian-Albrechts-Universität zu Kiel, Germany, *S.V. Roth,* Deutsches Elektronensynchrotron DESY, Germany, *P. Müller-Buschbaum,* Technische Universität München, Germany

With their easy processability, high flexibility and tuneable optical properties, organic electronics (OE) offer a wide range of potential applications. Especially photoactive polymers have received attention in recent years as candidates for organic photovoltaics (OPV) and light emitting diodes (OLEDs). Although based on organic materials, their electrodes are typically made from metals due to their unrivaled electronic conductivity. Thus, polymer-metal interfaces are inherently present in most OE devices and have a major influence on their behavior. Understanding the growth mechanisms of metal contacts on polymer thin films plays a crucial role in identifying potential ways to enhance the device performance. We investigate the morphological changes happening at the metal-polymer interface during the sputter deposition of metal contacts onto photoactive polymer films via in-situ grazing incidence small and wide angle x-ray scattering (GISAXS/GIWAXS) [1]. These techniques allow insights into the structural evolution of the metal on the organic film, which depends on various parameters such as the deposition rate or the film morphology. Making use of the brilliant synchrotron light source Petra III at DESY [2], we can study the deposition behavior of the metal on the polymer film with outstandingly high spatial and temporal resolution. The acquired large data sequences are tracked in real-time and further analyzed using the fast data reduction software DPDAK [3]. The final film morphology is characterized via scanning electron microscopy and X-ray reflectometry. UV/Vis absorption and reflection measurements complete our work. The metal layer formation can be described by applying an appropriate growth model based on our earlier work. [4] The model is refined in an iterative process of GISAXS simulations and data fitting. Comparing the deposition behavior of typical electrode materials on thin films of photoactive organic materials helps to understand their influence on the respective device performance.

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## Advanced Surface Engineering Division
## Room: 11 - Session SE+2D+NS+SS+TF-WeA

### Nanostructured Thin Films and Coatings

**Moderators:** Jianliang Lin, Southwest Research Institute, Matjaz Panjan, Jozef Stefan Institute, Slovenia

2:20pm **SE+2D+NS+SS+TF-WeA1 Plasma Process Development and Optimized Synthesis of TiB$_2$ Coatings from DC Magnetron Sputtering, High Power Impulse Magnetron Sputtering, and DC Vacuum Arc**, ***Johanna Rosen***, Linköping University, Sweden **INVITED**

The use of high power impulse magnetron sputtering (HiPIMS) or cathodic arc for the synthesis of TiB$_2$ coatings will drastically increase the amount of ionized species impinging on the substrate compared to regular DC magnetron sputtering. In particular for HiPIMS, it is possible to control the flux of ionized species by varying the pulse frequency, which allows exploration of the effect of ion to neutral flux ratio on the coating microstructure while keeping the substrate bias potential constant.

We show that the additional energy supplied during film growth in the HiPIMS process, compared to regular DC sputtering, results in a change from a randomly oriented polycrystalline microstructure to a 001-textured nanocolumnar structure. The change in preferred orientation also influence the hardness, which is enhanced from 36 GPa to ≥ 42 GPa. A further increase in the ion flux to the substrate leads to denser coatings with a higher residual compressive stress. Furthermore, we show that the energy supplied to the film surface is influenced by when the bias is applied relative to the HiPIMS pulse. Based on charge-state-resolved plasma analysis it is found that by applying the bias in synchronous with the HiPIMS pulse, a higher fraction of $B^+$ ions will constitute the total flux of bombarding ions. This results in a lower residual stress compared to coatings deposited under bombardment of mainly $Ar^+$ ions.

Finally, we also present results from TiB2 synthesis based on DC vacuum arc, and a route for attaining a stable, reproducible, and close to fully ionized plasma flux of Ti and B by removal of the external magnetic field. Plasma analysis shows increased ion charge states as well as ion energies compared to HiPIMS. Furthermore, while regular DC magnetron sputtering and HiPIMS typically give a B to Ti ratio above 2, the arc deposited coatings have a stoichiometry close to 2. Despite observations of macroparticle generation during synthesis, the film surface is very smooth with a negligible amount of particles.

3:00pm **SE+2D+NS+SS+TF-WeA3 Multi-technique Approach for Studying Co-sputtered M-Si-O Thin Films**, ***Lirong Sun***, General Dynamics Information Technology, *N.R. Murphy*, Air Force Research Laboratory, *J.T. Grant*, Azimuth Corporation

In this work, the M-Si-O thin films (M: Al and Ta) were prepared through reactive pulsed DC magnetron co-sputtering of M and Si targets in an $O_2$/Ar mixture. The M fraction [M/(M+Si)] of different chemical compositions ($M_xSi_yO_z$), as determined through X-ray photoelectron spectroscopy (XPS), was varied between 0 and 100% by changing sputtering power applied to the M targets. The film thickness, refractive index (n) and extinction coefficient (k) were determined by *in situ* spectroscopic ellipsometry (*i*SE). Concurrent with ellipsometry measurements, the *in situ* stress evolution of the films, as correlated to the M fraction, was investigated using a multi-beam optical sensor (MOS) system. The MOS system was used to measure both intrinsic stress resulting from the deposition process as well as thermal stress evolved during heating/cooling process. Data obtained through stress monitoring during heating and cooling was used to calculate the coefficient of thermal expansion (CTE). The density and crystallinity of the films were measured by X-ray diffraction and X-ray reflectivity, respectively. Transmission and reflectance of the films were carried out by UV-Vis-NIR spectroscopy. Finally, this study derives a process-property-microstructure relationship correlating the optical constants, CTE, intrinsic stress, and M fraction.

3:20pm **SE+2D+NS+SS+TF-WeA4 Ultra-high Vacuum Magnetron Sputter-deposition of Zr/Al$_2$O$_3$(0001): Effect of Substrate Temperature on Zr Thin Film Microstructure and Thermal Stability of Zr-Al$_2$O$_3$ Interfaces**, *K. Tanaka, J. Fankhauser*, University of California at Los Angeles, *M. Sato*, Nagoya University, Japan, *D. Yu, A. Aleman, A. Ebnonnasir, C. Li*, University of California at Los Angeles, *M. Kobashi*, Nagoya University, Japan, *M.S. Goorsky*, ***Suneel Kodambaka***, University of California at Los Angeles

Zr thin films are grown on $Al_2O_3$(0001) substrates in an ultra-high vacuum deposition system via dc magnetron sputtering of Zr target in Ar atmosphere at temperatures $T_s$ between 600 ºC and 900 ºC. The as-deposited layer surface structure and composition are determined *in situ* using low-energy electron diffraction and Auger electron spectroscopy, respectively. Bulk crystallinity and microstructures of the samples are determined using x-ray diffraction, cross-sectional transmission electron microscopy along with energy dispersive spectroscopy. At 600 ºC $\leq T_s <$ 750 ºC, we obtain fully dense, hexagonal close-packed structured Zr(0001) thin films with smooth surfaces. At $T_s \geq$ 750 ºC, the Zr layers are porous, exhibit {0001} texture, and with rough surfaces. Energy dispersive x-ray spectra obtained from the Zr/$Al_2O_3$ interfaces reveal the formation of Zr-Al intermetallic compounds, whose thickness increases exponentially with increasing $T_s$. We attribute the formation of this interfacial layers to fast diffusion of Zr and reaction with the $Al_2O_3$ substrate.}

4:20pm **SE+2D+NS+SS+TF-WeA7 Structural, Mechanical, Optical Properties of Molybdenum Incorporated β-Ga$_2$O$_3$ Nanocrystalline Films for Extreme Environment Applications**, ***Anil Battu***, *S. Manandhar, C.V. Ramana*, University of Texas at El Paso

Recently, gallium oxide ($Ga_2O_3$) has been attracting the attention of researchers as a suitable material for different extreme environment applications, such as high power electronics, optoelectronics, ultraviolet transparent conductive oxides, and gas sensors. β-$Ga_2O_3$ exhibits the highest thermal and chemical stability, which makes the material interesting for high-temperature oxygen sensor applications. However, the response time and sensitivity must be improved. In recent years, doping $Ga_2O_3$ with the suitable metal ions has been considered to alter the electronic properties and to improve sensor performance. In this context, the present work was performed on using a mechanically resilient metal (Mo) to incorporate into Ga-oxide (GMO) to provide excellent physical and thermo-mechanical characteristics. The GMO nanocomposite films with variable Mo contents (0-11.23 at%) were sputter-deposited onto Si(100) by varying the sputtering power in the range of 0-100 W. The effect of Mo on the crystal structure, mechanical properties and optical properties of GMO nanocomposite films is significant. While Mo content ≤ 4 at% reatins the β-$Ga_2O_3$ phase, higher Mo content induces amorphization. Molybdenum incorporation into β-$Ga_2O_3$, reduces the grain-size leading to amorphous nature of the entire film as well as surfaces. The nanoindentation studies indicate the remarkable effect of structural evolution and Mo content on the mechanical properties of the deposited GMO thin films. While Mo incorporation increases the hardness from 25 to 36 GPa, elesatic modulus decreases. Mo-induced red-shift in the band gap is significant in GMO films. Based on the results, a structure-property relationship in established in Mo incorporated $Ga_2O_3$ films.

4:40pm **SE+2D+NS+SS+TF-WeA8 Investigating Mass Transport and other Events underlying Rapid, Propagating Formation Reactions in Pt/Al Multilayer Films**, ***David Adams***, *M.J. Abere, C. Sobczak, D.E. Kittell, C.D. Yarrington, C.B. Saltonstall, T.E. Beechem*, Sandia National Laboratories

Metallic thin film multilayers that undergo rapid, self-propagating exothermic reactions are of interest for several applications including advanced joining technology. Reactive multilayers, such as commercially available Ni-Al, have been developed as a heat source to locally solder or braze dissimilar materials. A local heating approach is of great benefit for joining temperature-sensitive components and metastable structures. The development of new materials for reactive joining requires an improved, detailed understanding of mass transport, chemical reactions, heat release and thermal transport processes. With this presentation, we describe recent studies of a more highly exothermic reactive multilayer system (Pt/Al). Thin Pt/Al multilayers exhibit rapid propagating reactions with flame speeds as high as 100 m/s and internal heating rates > $1x10^7$ K/s. Equimolar designs are characterized by a substantial heat of formation, ~100 kJ/mol. at., which is approximately twice that of Ni/Al. Our discussion of equimolar Pt/Al multilayers will focus on the thermal and mass transport characteristics which underly their self-propagating reactions. We have utilized advanced thin film characterization techniques to probe the thermal conductivity of different

Pt/Al multilayers having various periodicities. This acquired information is used within the framework of an analytical method developed by Mann et al. (J. Appl. Phys. 1997) to estimate the mass transport properties of Pt/Al multilayers subjected to high heating rates. The analytical model accounts for layer thicknesses, compositional profiles near interfaces, flame temperatures, heats of reaction, and adiabatic temperatures in order to predict reaction wavefront velocity and its variation with multilayer design.

This work was supported by a Sandia Laboratory Directed Research and Development (LDRD) program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

5:00pm **SE+2D+NS+SS+TF-WeA9 Adaptive Ceramic Coatings for Extreme Environments**, ***Samir Aouadi***, University of North Texas, *C. Muratore*, University of Dayton, *A.A. Voevodin*, University of North Texas **INVITED**

This talk will provide an overview of the latest research developments in the design and exploration of hard coatings with high temperature adaptive behavior in tribological contacts. The initial focus of the talk will be on understanding the major mechanisms that lead to a reduction in friction and/or wear in high temperature lubricious oxides. Adaptive mechanisms will also be discussed and will include metal diffusion and formation of lubricant phases at worn surfaces, thermally- and mechanically-induced phase transitions in hexagonal solids, contact surface tribo-chemical evolutions to form phases with low melting point, and formation of easy to shear solid oxides. All of these adaptive mechanisms are combined in nanocomposite coatings with synergistic self-adaptation of surface structure and chemistry to lubricate from ambient temperatures to 1000 °C and provide surface chemical and structural reversibility during temperature cycling to maintain low friction coefficients. Changes in the structural and chemical properties of these materials as a function of temperature will be correlated to their mechanical and tribological performance using a range of experimental tools in addition to simulations based on *ab initio* calculations and molecular dynamics simulation methods. This review also includes a discussion of the industrial applications of these coatings as well as of potential improvements to the coating design and other anticipated future developments.

5:40pm **SE+2D+NS+SS+TF-WeA11 Ultralow Wear of Stable Nanocrystalline Metals**, ***Nicolas Argibay***, *T.A. Furnish, T.F. Babuska, C.J. O'Brien, J.F. Curry, B.L. Nation, A.B. Kustas, P. Lu, M. Chandross, D.P. Adams, M.A. Rodriguez, M.T. Dugger, B.L. Boyce, B.G. Clark*, Sandia National Laboratories

The existence of intrinsic thermodynamically stable nanocrystalline binary metal alloys has been recently proposed and supported by demonstrations of stability through annealing of powders. There is a great deal of interest in understanding the impact of mechanical stress on this stability. In this presentation we discuss the results of an investigation on the stress and temperature dependent stability of a nanocrystalline noble-metal alloy (Pt-Au) in the form of sputtered thin films. We show that stabilization of nanocrystalline structure can impart low friction (μ ~ 0.2-0.3) and remarkable wear resistance, 100x lower than any previously reported metal.

6:00pm **SE+2D+NS+SS+TF-WeA12 From Ab-Initio Design to Synthesis of Multifunctional Coatings with Enhanced Hardness and Toughness**, ***Daniel Edström***, *D. Sangiovanni, L. Hultman, I. Petrov, J. Greene, V. Chirita*, Linköping University, University of Illinois at Urbana-Champaign

Enhanced toughness in hard and superhard thin films is a primary requirement for present day ceramic hard coatings, known to be prone to brittle failure. Density Functional Theory (DFT) investigations predicted significant improvements in the toughness of several B1 structured transition-metal nitride ( TMN ) alloys, obtained by alloying TiN or VN with MoN and WN. The calculations reveal that the electronic mechanism responsible for toughness enhancement stems from the high valence electron concentration (VEC) of these alloys, which leads to the formation of alternating layers of high/low charge density orthogonal to the applied stress, and allows a selective response to deformations. This effect is observed for ordered and disordered ternary TMN alloys. The essential feature in the disordered alloys, as reported for ordered alloys, is the increased occupancy of electronic d-$t_{2g}$ metallic states, which allows the selective response to tensile/shearing stresses, and explains the enhanced toughness confirmed experimentally for VMoN films.

Recently, these results have been validated experimentally. Single-crystal VMoN alloys, grown by dual-target reactive magnetron sputtering together with VN and TiN reference samples, exhibit hardness > 50% higher than that of VN, and while nanoindented VN and TiN reference samples suffer from severe cracking, the VMoN films do not crack.

New DFT calculations suggest similar toughness improvements may be obtained in pseudobinary NaCl structured transition-metal carbide (TMC) compounds by alloying TiC or VC with WC and MoC. A comprehensive electronic structure analysis, as well as stress/strain curves DFT-based calculations, carried out for the newly formed ternary TMC alloys, reveal similar trends between shear-stressed TMN and TMC compounds, and predict VMoC as the best candidate alloy with enhanced ductility.

KEYWORDS: nitrides, carbides, toughness, hardness, ductility.

## Surface Science Division
## Room: 25 - Session SS+HC+NS-WeA

## Dynamical Processes at Surfaces
**Moderators:** Ashleigh Baber, James Madison University, Kathryn Perrine, Michigan Technological University

3:00pm **SS+HC+NS-WeA3 Quantum Molecular Machines**, ***Saw-Wai Hla***, Ohio University and Argonne National Laboratory **INVITED**

One of the goals of nanotechnology is the development of complex molecular machines that can be operated with atomic level control in a solid-state environment. Most biological molecular machines have the sizes from tens of nanometers to a few microns –a range where classical machine concepts hold. However, artificially designed molecular machines can be in the size range down to a few nanometers or less, which is in the range of quantum processes. In this talk, we will present various artificial molecular machines such as molecular motors and linear transport devices such as molecular cars operating in the quantum regime on materials surfaces. Fundamental operations of these synthetic molecular machines are investigated at one molecular machine-at-a-time in an atomically clean environment using low temperature scanning tunneling microscopy (STM), tunneling spectroscopy, and molecular manipulation schemes [1,2]. These investigations reveal how charge and energy transfer are taken place within single molecular machines as well as among the molecular machines in the molecular networks. Moreover by introducing dipole active components in the rotor arms of the molecular motors, communication among the molecules can be introduced via dipolar interaction. In addition to single molecule operations, synchronization of molecular motors can be achieved depending on the symmetry of the molecular assemblies on surfaces and the strength of applied electric field energy. Here, all the molecular motors can be rotated in a synchronized manner using 1V or higher electric field supplied from the STM tip. Below this bias, the rotor arms of the molecular motors can reorient into different directions. Careful analyses reveal that such reorientations of the molecular motors are not random, but they are coordinated to minimize the energy. Furthermore, individual molecular motors can be charged using the inelastic tunneling scheme with the STM tip. This introduces spin-active components within the molecular motors and enables us to investigate spintronic properties of individual molecular motors at the sub-molecular scale using tunneling spectroscopy. For the controlled linear transport at the nanoscale, we will present the latest development of molecular nanocars.This work is supported by US DOE grant DE-FG02-02ER46012.

[1] U.G.E. Perera . F. Ample, H. Kersell, Y. Zhang, G. Vives, J. Echeverria, M. Grisolia, G. Rapenne, C. Joachim, and S.-W. Hla. ***Nature Nanotechnology 8***, 46-51(2013).

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4:20pm **SS+HC+NS-WeA7 Collective, Multi-atom Diffusion in Epitaxially Grown Metallic Films**, ***Matt Hershberger***, *M. Hupalo, P.A. Thiel*, Iowa State University Ames Laboratory –USDOE, *M.K.L. Man, M.S. Altman*, Hong Kong University of Science and Technology, Hong Kong, *C.H. Mullet, S. Chiang*, University of California-Davis, *M.C. Tringides*, Iowa State University Ames Laboratory –USDOE

Surface diffusion is the main process controlling mass transport of many important phenomena such as nucleation, nanostructure growth, pattern formation, and chemical reactions. In practically all cases, it is described as a random walk of independently moving adatoms. Such process is inherently stochastic and therefore very slow as a route to self-organization in nature.

A series of experiments in different epitaxially grown metallic films over the last 5 years using different techniques has challenged the classical picture. The experiments have shown unusually fast, collective diffusion is present in nature, observed in a range of experiments over different length and time scales.

STM experiments show that fully completed Pb crystalline islands emerge "explosively" out of the compressed wetting layer on Si(111) after a critical coverage $q_c$=1.22ML is reached. The unexpectedly high island growth rates and directional correlations show that mass transport is through the correlated motion of the wetting layer.[1] Additional deposition of Pb shows island density that does not reach steady state; it shows abrupt jumps in island density with new generations of smaller islands continuing to nucleate (in contrast to classical nucleation). Real time experiments with LEEM, monitoring the refilling of an initial vacant area in Pb/Si(111), show that the initial steep profile does not disperse and that the profile propagates at constant velocity x~t. The profile follows a non-Fickian form with two moving highly correlated fronts, one inward and the other outward.[2] The formation of long anisotropic multi-height Ag islands on Ge(110) is exceedingly fast, when compared to the rates expected from random walk Ag diffusion barriers. A wetting layer is also present prior to the crystallization and is responsible for the fast growth rates, although the temperature is above room temperature.[3] Evidence for collective diffusion has been seen in Pb/Si(100), Pb/Ge(111), Pb/Ni(111), Pb/W(110), Ag/Si(110).

A better understanding of these processes can guide the search of collective transport in other systems, especially to identify the relevant growth "window" (of temperature and coverage). It can further clarify the role of stress since the compression of the non-crystalline wetting layer is critical for these effects.[4]

References:

1. M. T. Hershberger et al., .Phys. Rev. Lett. 113, 236101 (2014)

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4. E. Granato et al., Phys. Rev. Lett. 111, 126102 (2013)

### 4:40pm **SS+HC+NS-WeA8 Quantitative Molecular Beam Study for $CO_2$ Hydrogenation on Cu (111) and Cu(100) Surfaces**, ***Jiamei Quan***, *T. Kondo, T. Kozarashi, T. Mogi, J. Nakamura*, University of Tsukuba, Japan

Catalytic conversion of $CO_2$ into valuable fuels and chemicals such as methanol, especially if activated by a precise energetic control, represents a potentially economic strategy for utilization of fossil feedstock and reducing $CO_2$ emissions and their contributions to climate changes. The formation of formate intermediates ($2CO_2 + H_2 \rightarrow 2H\ COO_a$) on Cu catalysts is an important initial step, in which the reaction probability is reported as low as $10^{-12}$ at 340 K.[1] Our previous reports suggested that the reaction proceeds via an Eley-Rideal type mechanism, where $CO_2$ directly reacts with pre-adsorbed H to form $HCOO_a$.[2] Recently, we have clarified using supersonic molecular beam apparatuses that the reaction probability is promoted up to $\sim 10^{-3}$ by increasing both translational and vibrational energies, while insensitive to the Cu surface structure (Cu(111) and Cu(100)) and the surface temperature (120 - 210K). The energy efficacy on the reaction probability is found to be larger as much as 100 times for the vibrational energy compared to the translational energy, suggesting that the vibrational excitation significantly enhances the formate formation. Based on the comparison with DFT calculations, we conclude that the excitation of the bending mode of $CO_2$ at the transition is crucially important to form the C-H bond of HCOO via lowering LUMO level of $CO_2$. The small pre-exponential factor derived by the experiment is ascribed to the preferential orientation of the $CO_2$ molecule (C-end collision to $H_a$ on Cu) for the reaction. The discovered thermal non-equilibrium channel in $CO_2$ conversion, which doesn't require the heating of catalysts, is expected to provide a prototypical surface reaction dynamics and open up novel industrial pathways of efficient $CO_2$ conversion into useful chemicals and fuels.

[1] (a) T. Fujitani, J. Nakamrua et al., *App. Surf. Sci.* 121–122 (**1997**) 583; (b) H. Nakano, J. Nakamrua et al., *J. Phys. Chem. B* 105 (**2001**) 1355.

[2] (a) J. Quan, J. Nakamrua, et al., Angew. Chem. Int. Ed. 56 (**2017**) 3496; (b) G. Wang, J. Nakamura, et al., *J. Phys. Chem. B* 110 (**2005**) 9.

### 5:00pm **SS+HC+NS-WeA9 A New Approach for Controlling the Rotational Orientation of a Molecule and Studying the Stereodynamics of a Molecule-Surface Collision**, ***Gil Alexandrowicz***, Technion – Israel Institute of Technology, Israel **INVITED**

The interaction between a molecule and a solid surface is fundamental to a huge variety of research fields and applications, ranging from industrial heterogeneous catalysis to ultra-cold astrochemical reactions on cosmic dust. One molecular property that affects molecule-surface interactions, but is also particularly difficult to control and resolve, is the orientation and alignment of the rotational axis of the molecule i.e. the quantum rotation projection states. The existing paradigm is that control over this molecular property can be obtained either by photo-excitation schemes and/or by deflecting experiments using strong electric or magnetic fields. Using these approaches valuable insight was obtained and the crucial role the rotation projection states have on the outcome of molecule-surface collision was demonstrated. However, the two approaches mentioned above can only be applied to a very small sub-group of systems (typically excited/paramagnetic species). In this presentation I will describe a completely different approach which utilizes the rotational magnetic moment, which is a general molecular property, to control and resolve the projection rotation states of ground-state molecules.

Our new experimental approach combines an atomic interference setup, originally built to perform ultra-fast surface diffusion measurements[1], with magnetic manipulation techniques we developed for separating quantum states of molecular beams[2]. The result is a unique setup which can both control and resolve the rotational orientation of a molecule as it collides with a solid surface. In this presentation I will show some recent experiments where we controlled the rotational orientation of a ground state hydrogen molecule, and correspondingly modified the outcome of a collision event with flat and stepped copper surfaces[3].The possibilities this new technique opens for studying the stereodynamic nature of molecule-surface interactions as well as ultra-fast surface dynamics will be briefly discussed.

[1] Progress in Surface Science, 84, 323 (2009).

[2] Science, 331, 319 (2011).

[3] Nature communications, (DOI: 10.1038/ncomms15357), in press (2017).

### 5:40pm **SS+HC+NS-WeA11 Surface Temperature Effects in $CH_4$ Dissociation on Flat and Stepped Nickel Single Crystals**, ***Eric High***, *E.K. Dombrowski, A.L. Utz*, Tufts University

A modified King and Wells molecular beam reflectivity method was used to obtain thermal and quantum state resolved initial sticking probabilities ($S_0$) for $CH_4$ on nickel single crystals at elevated surface temperatures (500 to 1000K). We recorded the reactivity of a supersonic molecular beam of methane with and without laser excitation to v=1 of the $v_3$ antisymmetric C-H stretching vibration. Square wave modulation of the laser source during $CH_4$ deposition provided simultaneous real-time measurement of $S_0^{LaserOff}$ and $S_0^{v3}$, resulting in a dramatic reduction in data acquisition time, a significant reduction in experimental error, and the opportunity to measure S as a function of accumulating surface coverage. On a Ni(111) surface, both laser-off and vibrational state-resolved measurements of $S_0$ were essentially independent of surface temperature, within error, from 1000 to 800K and then decreased linearly as $T_{surf}$ dropped from 800 to 500K. These findings are consistent with the predictions of Reaction Path Hamiltonian calculations by Jackson and Guo over a wide range of incident kinetic energies (96 to 167 kJ/mol). The calculations suggest that at low incident energies, reactivity occurs predominantly at on-top sites, but as energy increases, reactions begin to occur at bridge sites as well. We will also present more recent measurements on the low step density Ni(997) surface that provide insight into the role of step-edge nickel atoms at these industrially relevant surface temperatures.

### 6:00pm **SS+HC+NS-WeA12 Experimental and Theoretical Study of Rotationally Inelastic Diffraction of $H_2(D_2)$ from Methyl-Terminated Si(111)**, ***Kevin Nihill****, *Z.M. Hund*, University of Chicago, *A. Muzas, C. Diaz, M. del Cueto*, Universidad Autónoma de Madrid, Spain, *T. Frankcombe*, University of New South Wales, Australia, *N. Plymale, N.S. Lewis*, California Institute of Technology, *F. Martin*, Universidad Autónoma de Madrid, Spain, *S.J. Sibener*, University of Chicago

Fundamental details concerning the interaction between $H_2$ and $CH_3$-Si(111) have been elucidated by the combination of diffractive scattering experiments and electronic structure and scattering calculations. Rotationally inelastic diffraction (RID) of $H_2$ and $D_2$ from this model hydrocarbon-decorated semiconductor interface has been confirmed for the first time *via* both time-of-flight and diffraction measurements, with modest $j = 0 \rightarrow 2$ RID intensities for $H_2$ compared to the strong RID features observed for $D_2$ over a large range of kinematic scattering conditions along two high-symmetry azimuthal directions. The Debye-Waller model was applied to the thermal attenuation of diffraction peaks, allowing for precise determination of the RID probabilities by accounting for incoherent motion of the $CH_3$-Si(111) surface atoms. The probabilities of rotationally inelastic diffraction of $H_2$ and $D_2$ have been quantitatively evaluated as a function of beam energy and scattering angle, and have been compared with complementary electronic structure and scattering calculations to provide insight into the interaction potential between $H_2$ ($D_2$) and hence the surface charge density distribution. Specifically, a six-dimensional potential energy surface (PES), describing the electronic structure of the $H_2(D_2)/CH_3$-Si(111) system, has been computed based on interpolation of density functional theory (DFT) energies. Quantum and classical dynamics simulations have allowed for an assessment of the accuracy of the PES, and subsequently for identification of the features of the PES that serve as classical turning points. A close scrutiny of the PES reveals the highly anisotropic character of the interaction potential at these turning points. This combination of experiment and theory provides new and important details about the interaction of $H_2$ with a hybrid organic-semiconductor interface, which can be used to further investigate energy flow in technologically relevant systems.

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* **Morton S. Traum Award Finalist**

## Tribology Focus Topic
## Room: 10 - Session TR+AS+HI+NS+SS-WeA

### Molecular Origins of Friction
**Moderators:** J. David Schall, Oakland University, Paul Sheehan, US Naval Research Laboratory

2:20pm **TR+AS+HI+NS+SS-WeA1 On the Stochastic Nature of Bonding in Contact: Simulations of Indentation and Sliding of DLC Tips on Diamond Surfaces**, ***J. David Schall***, Oakland University, *R.A. Bernal*, University of Texas at Dallas, *Z. Miline*, University of Pennsylvania, *P. Chen, P. Tsai, Y.-R. Jeng*, National Chung Cheng University, Taiwan, Republic of China, *K.T. Turner, R.W. Carpick*, University of Pennsylvania, *J.A. Harrison*, United States Naval Academy

Contact at the nanoscale has important implications in the use of tip-based nanomanufacturing, data storage, and imaging with scanning probes. Tip wear reduces predictability in manufacturing and image quality such scanning probe applications. As a means to reduce wear, hard wear-resistant materials such as diamond-like carbon (DLC), ultra nanocrystalline diamond (UNCD) and amorphous carbon (a-C:H) have been used to coat scanning probe tips. Understanding of the behavior of these materials in contact is critically important towards their successful application. Recent studies using a TEM nanoindenter showed significant variation in both pull-in and pull-off forces obtained during the repeated indentation of a DLC tip on to a diamond surface. Furthermore, the pull-in and pull-off forces do not appear to be correlated. In this presentation, results from molecular dynamics simulations of a DLC tip on hydrogen terminated diamond surfaces will presented. The tip was constructed with a structure and geometry similar to that of the tip used in experiment. The resulting simulations show that the pull-in force appears to be dominated by long range dispersion forces while the pull-off force is determined by the number of covalent bonds formed during the contact. For a given surface, the formation of bonds during indention appears to be a stochastic process with multiple indents of the same tip at the surface same location showing a widely varying number of bonds formed. It is therefore hypothesized that the variation in pull-off forces observed in experiment are also related to the number of bonds formed across the tip-surface interface.

**Supported by **The National Science Foundation and the Air Force Office of Scientific Research**

2:40pm **TR+AS+HI+NS+SS-WeA2 New Insights about the Fundamental Mechanisms of Friction of $MoS_2$**, ***John Curry***, Lehigh University, *M. Wilson, T.F. Babuska, M. Chandross*, Sandia National Laboratories, *H. Luftman, N.C. Strandwitz, B.A. Krick*, Lehigh University, *N. Argibay*, Sandia National Laboratories

Molybdenum Disulfide ($MoS_2$) is a solid lubricant used widely in aerospace applications, capable of providing ultralow friction (coefficients, $\mu < 0.01$) in inert environments such as the vacuum found in outer space. Research over the years has led to the development of $MoS_2$ nanocomposites that are less susceptible to the effects of environment and aging. Yet, the fundamental mechanisms responsible for environmental sensitivity and degraded friction behavior remain highly debated. Tribological experiments and molecular dynamics (MD) simulations were used to understand the evolution of friction behavior for $MoS_2$ coatings as a function of temperature, lattice commensurability and defect density. The oxidative resistance of $MoS_2$ coatings prepared with differing degrees of defect density and basal orientation was also assessed via high-sensitivity low-energy ion scattering (HS-LEIS) depth profiling, X-ray photoelectron spectroscopy (XPS), tribological experiments and MD. Through these findings, we discuss new connections between atomic-scale mechanisms and macro-scale friction behavior of this class of lubricant in a wide range of environments.

3:00pm **TR+AS+HI+NS+SS-WeA3 The Influence of Environmental Exposure and the Substrate on the Lubricating Properties of Two-Dimensional Materials**, *P. Gong*, University of Calgary, Canada, *Z. Ye*, Miami University, *L. Yuan*, ***Philip Egberts***, University of Calgary, Canada **INVITED**

The friction reducing properties of graphene has been shown to have a number of interesting properties, such as a dependence on the number of layers of the lubricant present, an exceptional dependence on the surface adhesion properties of the underlying substrate, and environmental stability. These properties have been attributed to its low mechanical strength to out-of-plane deformation, its innate thinness, and the influence of the environment on the surface energy. In this work, the friction reducing properties of graphene are examined using experiments and simulation. In particular, the influence of surface energy and associated wettability of graphene are explored as a property that can influence the lubrication properties of graphene, but also friction hysteresis. While little to no variation in pull-off forces have been observed on varying numbers of graphene covering the surfaces in experiments, the impact of the variance of surface energy on friction, and in particular friction under humid environments, suggests that surface energy may have a stronger influence on graphene's friction reducing ability than suggested in previous work.

4:20pm **TR+AS+HI+NS+SS-WeA7 Fundamental Understanding of Interfacial Adhesion and Tribochemistry by Ab Initio Calculations**, ***M.Clelia Righi***, University of Modena and Reggio Emilia, Italy **INVITED**

Tribologically-induced chemical modifications of surfaces interacting with lubricant additives or other molecules present in the environment surrounding the sliding media can substantially change the adhesion and friction of materials in contact. Therefore, is highly desirable to understand how they take place. However, tribochemical reactions are difficult to monitor in real-time by experiments, which leaves a gap in the atomistic understanding required for their control.

We apply *ab initio* molecular dynamics to monitor chemical reactions involving common solid lubricants, namely molybdenum disulfide, graphene/graphite and carbon-based films, interacting with water molecules in the presence of mechanical stresses. Our simulations elucidate atomistic mechanisms relevant to understand the effects humidity on the lubricating properties of these materials.[1,2]

As second issue, we investigate the tribochemistry of sulfur, phosphorus and graphene on iron and discuss the role of metal passivation in reducing the interfacial adhesion and shear strength. We generalize the result by establishing a connection between the tribological and the electronic properties of interfaces. This adds a new piece of information for the ultimate understanding of the fundamental nature of frictional forces. [3,4]

[1] P. Restuccia, G. Levita and M. C. Righi *Graphene and MoS2 interacting with water: a comparison by ab initio calculations* Carbon 107, 878 (2016).

[2] S. Kajita and M. C. Righi*A fundamental mechanism for carbon-film lubricity identified by means of ab initio molecular dynamics*, Carbon 103, 193 (2016).

[3] M. C. Righi, S. Loehlé, M. I. De Barros Bouchet, S. Mambingo-Doumbeand J. M. Martin *A comparative study on the functionality of S- and P-based lubricant additives by combined first principles and experimental analysis* RSC Advances, 6, 47753 (2016).

[4] P. Restuccia and M. C. Righi *Tribochemistry of graphene on iron and its possible role in lubrication of steel* Carbon 106, 118 (2016).

5:00pm **TR+AS+HI+NS+SS-WeA9 Friction Between 2D Solids during Lattice Directed Sliding**, ***Paul Sheehan***, US Naval Research Laboratory, *CM. Lieber*, Harvard University

Nanometer-scale crystals of the 2D oxide molybdenum trioxide ($MoO_3$) were formed atop the transition metal dichalcogenides $MoS_2$ and $MoSe_2$. The $MoO_3$ nanocrystals are partially commensurate with the dichalcogenide substrates, being aligned only along one of the substrate's crystallographic axes. These nanocrystals can be slid only along the aligned direction and maintain their alignment with the substrate during motion. Using an AFM probe to oscillate the nanocrystals, it was found that the lateral force required to move them increased linearly with nanocrystal area. The slope of this curve, the interfacial shear strength, was significantly lower than for macroscale systems. It also depended strongly on the duration and the velocity of sliding of the crystal, suggesting a thermal activation model for the system. Finally, it was found that lower commensuration between the nanocrystal and the substrate increased the interfacial shear, a trend opposite that predicted theoretically.

5:40pm **TR+AS+HI+NS+SS-WeA11 Single Molecule Force Measurement: Mechanic and Symmetry Dependent Lateral Force**, ***Yuan Zhang***, Argonne National Laboratory, *S. Khadka*, Ohio University, *B. Narayanan, A. Ngo*, Argonne National Laboratory, *Y. Li*, Ohio University, *B. Fisher, L. Curtiss, S. Sankaranarayanan, S.W. Hla*, Argonne National Laboratory

Mechanical properties of molecules adsorbed on materials surfaces are increasingly vital for the applications of molecular thin films as well as for the fundamental understanding of quantum friction. Here, we employ atomic/molecular manipulation schemes to investigate mechanic and symmetry dependent lateral diffusion processes of individual molecules on various substrates using a combined scanning tunneling microscope (STM) and q+ atomic force microscopy system at low temperature and in ultrahigh vacuum environment. Lateral force measurements of individual sexiphenyl, an oligomer type molecule, exhibits an interesting friction behavior originated from the symmetry of the molecule-substrate system. We found ~160% increase in the lateral force during the diffusion of the molecule across a Ag(111) surface depending on the long molecular axis alignment on the surface. A comparison of the shape and symmetry dependent molecular diffusion process is realized by manipulating cobalt-porphyrin molecules on aAu(111) surface. The results are in full agreement with molecular dynamic simulations. In addition, we will also discuss atomic and molecular level force measurement using an STM tip, which opens simultaneous electronic, structural and force measurements at the single atom and molecule level.

## Vacuum Technology Division
## Room: 20 - Session VT-WeA

## The History and Future of Materials, Surfaces and Interfaces (ALL INVITED SESSION)

**Moderators:** Gregory Exharos, Pacific Northwest National Laboratory, Amy Walker, University of Texas at Dallas

2:20pm **VT-WeA1 The 14-billion Year History of the Universe Leading to Modern Materials Science**, ***Joe Greene***, University of Illinois **INVITED**

The story of our universe begins approximately 13.8 billion years ago with the Big Bang. Many of the formative events occurred in the first tiny fractions of a second (the universe evolved from consisting of a quark/gluon plasma to form the first protons and neutrons) to minutes (free neutrons decay to electrons and neutrinos) to a few tens of thousands of years (elementary particles form the first elements, which leads to the development of stars due to local density fluctuations). Planet Earth nucleated and began to accrete interstellar debris ~4.5 billion years ago. While the lighter metal elements on earth formed primarily due to stellar supernovae explosions, the primary mechanism leading to the formation of the heavier elements has only recently been demonstrated. The first known sophisticated stone tools used by hominids date to 2.6 million years ago.

Gold is likely the first metal discovered by man, >11,000 years ago. However, unlike copper (~9000 BC), bronze (~5000 BC), and cast iron (~600 BC), it was too soft for fabrication of tools and weapons. Instead, gold was used for decoration, religious artifacts, and commerce. The earliest high-purity Au artifacts derive from NE Bulgaria ~6500 y ago; however, the largest known concentration of ancient gold mines is in the Egyptian Eastern Desert. Copper extraction from ore was already being carried out in the Balkans (E Serbia and S Bulgaria) ~7500 years ago. Spectacular copper sculptures displaying very high levels of metallurgical and artistic craftsmanship have been found in Mesopotamia (S Iraq).

Gold brazing of metal parts was first reported ~3400 BC in Sumaria. The earliest documented thin films were gold layers, some < 1000 Å thick, produced by Egyptians ~5000 years ago. Examples, gilded on copper and bronze statues and artifacts (requiring sophisticated compositionally-graded interfacial adhesion layers), were found in pyramids dating to ~2650 BC. Electroless gold and silver plating was developed much later by the Moche Indians of Peru in ~100 BC.

Early biomaterials, used as human prosthetics following successful amputations, date to 950 BC in Egypt; while the first nano-based devices, exhibiting spectacular dichroic effects due to ~200-Å-diameter Au quantum dots, were synthesized in Rome ~350 AD.

Vapor-phase deposition of thin films required the invention of vacuum pumps (~1650 through 1865). The fascinating development of crystallography begins with Plato in 360 BC.

While an historical road map tracing the progress of materials technology is interesting in itself, the stories behind these developments are even more remarkable and provide insight into the evolution of scientific reasoning.

4:20pm **VT-WeA7 Controlling Microorganisms with Bio-inspired Materials**, ***Caitlin Howell***, University of Maine

Nature was the first to create adaptive, multi-functional materials, surfaces, and interfaces. Now, the concept of borrowing ideas from Nature is one of the major drivers in the future of materials- and surface-based technology. In keeping with this trajectory, our group designs surfaces to understand and control microorganisms using bio-inspired concepts. One major application is in the control of bacterial adhesion leading to biofilm formation, which causes a wide range of problems in industry and medicine. Using a method inspired by the *Nepenthes* pitcher plant, which uses a thin immobilized layer of water to repel insects, we can create selective patterns of bacterial adhesion using common laboratory materials and simple bench-top surface treatments. Inspired by the vascular systems of plants and animals, we can then make these surfaces continuously self-replenishing by embedding channels within the material itself. The channels are then filled with excess liquid, which can diffuse to the surface and heal depleted or damaged areas. Finally, we are working to develop these materials on paper substrates to create low-cost, lightweight pathogen-handling materials for use in diagnostics or analytics. Through this work, we aim to develop new and versatile tools for the exploration and control of microorganisms.

4:40pm **VT-WeA8 Comparison of Oxygen Adsorption and Absorption on Rhodium, Silver, and Stepped Platinum Surfaces**, ***Daniel Killelea***, *R.G. Farber, M.E. Turano,* Loyola University Chicago, *E.V. Iski,* University of Tulsa, *L.B.F. Juurlink,* Leiden Institute of Chemistry, The Netherlands, *J. Derouin*, Loyola University Chicago

The interaction of oxygen with the surfaces of catalytically active transition metals has attracted much interest because of the relevance to heterogeneous catalysis. Recently, we have shown that oxygen coverages in excess of 1 ML are achievable using gas-phase atomic oxygen (AO) to dose the metal surfaces. This talk will discuss some recent results comparing the uptake of AO and $O_2$ on Ag(111), Rh(111), and stepped Pt surfaces. On Pt surfaces, the geometry of the monoatomic steps determines whether or not low temperature dissociative chemisorption of $O_2$ will occur. In addition, on Pt(553), prolonged exposure to AO does not result in O coverages in excess of a monolayer, suggesting the defects are not effective at promoting the formation of subsurface oxygen. Conversely, on Rh(111), subsurface oxygen readily forms from exposure to AO. Finally, the uptake of oxygen on Ag(111) is discussed; unlike Pt(553) or Rh(111), where little surface reconstruction occurs, Ag(111) undergoes several phase transformations as the oxygen coverage is increased. These results using AO demonstrate that UHV-compatible dosing can prepare the same surfaces resulting high pressure $O_2$ exposures, allowing for quantitative and structural analysis of the oxidized surfaces.

5:00pm **VT-WeA9 Single Asperity Contact and Sliding**, ***Ashlie Martini***, University of California Merced

Abstract: Nanoscale probes are widely used for surface and material characterization as well as for emerging nanoscale manufacturing techniques; they also are model single asperities and so provide a means of studying contact and relative motion between surfaces at a fundamental level. The challenge in understanding such phenomena is that experimentally-observed properties are determined by processes that occur within the interface between two materials. As such, it is desirable to complement experiments with simulations that can provide insight into the atomic-scale mechanisms within that buried interface. However, there are challenges to modeling nanoscale probe-based experiments with sufficient accuracy that the simulations can be used to explain experimental observables. We have addressed this issue in recent work by designing models to reproduce specific experiments in which nanoscale probes are used to characterize contact, friction and wear. We focus on tractable problems for which optimally-matched simulations can be directly validated by comparison to experiments and the simulations can in turn provide insight into the fundamental mechanisms underlying contact and sliding at the nanoscale.

5:20pm **VT-WeA10 Structure of Sub-nm Oxides Synthesized by Atomic Layer Deposition: From Isolated Cations to the Emergence of Crystallinity**, ***Angel Yanguas-Gil***, Argonne National Laboratory

The history of the AVS has witnessed a dramatic reduction in thickness of thin film materials. Characteristic dimensions of the order of a nanometer are commonplace for a wide range of applications, from energy storage to semiconductor processing, nanostructured photovoltaics, catalysis or beyond Von Neumann computing architectures. This has greatly reduced our margin of error in terms of achieving the right microstructure and properties as well as the long-term stability of materials, particularly when the synthesis takes place at low temperatures and the mobility of surface species is low.

Atomic layer deposition is a thin film technique that is well known for its ability to coat high surface area materials, but it also allows us to grow materials with extremely high precision and high reproducibility. This makes it an ideal model system to understand some of the fundamental aspects of the growth of materials at the nanometer scale and their stability with time and under extreme environments. In this talk I will show how through the combination of different in-situ techniques, from PDF to XAFS and FTIR, the ability to modulate surface reactivity, simulation and theory, we can study the evolution of the structure of materials from isolated cations to a bulk-like structure and isolate the main factors driving the evolution of microstructure. Looking into the future, the development of new in-situ characterization tools at synchrotron radiation facilities worldwide is going to be an enabling capability that will help us understand the driving forces behind the emergence of crystallinity at low temperatures.

5:40pm **VT-WeA11 The Power of Atomic Layer Deposition – Moving Beyond Amorphous Films**, ***Virginia Wheeler***, *A.C. Kozen, B.P. Downey, M. Currie, N. Nepal,* U.S. Naval Research Laboratory*, L.O. Nyakiti,* Texas A&M University*, D.J. Meyer, D.R. Boris, S.G. Walton, C.R. Eddy, Jr.,* U.S. Naval Research Laboratory

Atomic layer deposition (ALD) has emerged as a powerful technique to produce a wide variety of thin film materials including metal oxides, nitrides, and metals for use in numerous applications. This method has become increasingly useful as device dimensions are reduced and complexity is increased often resulting in non-planar architectures. The sequential, self-limiting reactions that define ALD enable excellent conformality on high-aspect ratio structures, angstrom level thickness control, and tunable film compositions. Additionally, ALD is conducted at low growth temperatures (Tg) which allows for integration of dissimilar materials as well as the ability to access new regions of phase diagrams in complex systems (ie. metastable phases, miscibility gaps, etc.). Traditionally, this low Tg yields amorphous films. In many applications, it is becoming increasingly advantageous to incorporate thin, conformal crystalline materials which are currently limited by the low Tg in ALD. To overcome this barrier, many have investigated post-deposition processing or plasma enhanced ALD. In this work, we will explore the advantages and limitations of approaches towards attaining crystalline ALD films through the following case studies: high quality phase transitions in ALD $VO_2$ and phase control of heteroepitaxial $Ga_2O_3$.

$VO_2$ is a thermochromic material that undergoes a crystalline phase change at critical temperature (68° C) resulting in drastic changes in optical and electrical properties. While crystallized ALD $VO_2$ films have been shown to have sufficient transitions, they are deposited amorphously. Crystalline films are only obtained through a post-deposition anneal (500-600° C in $O_2$) since the vanadium precursor degrades at elevated temperatures (>150° C). However, this high temperature anneal limits the integration of ALD $VO_2$ films with other materials and without careful consideration of anneal parameters such as temperature, pressure and gas environment can alter the stoichiometry and structure of the initial ALD $VO_2$ film.

A plasma enhanced ALD (PE-ALD) process was used to attain heteroepitaxial $Ga_2O_3$ films on c-plane sapphire substrates at 350° C. This is about half of traditional CVD or MBE methods, showing the benefits of PE-ALD. Furthermore, the crystallinity and phase composition of the $Ga_2O_3$ film can be control with growth temperature, plasma gas flow, and pressure. For example, reducing the chamber pressure an order of magnitude resulted in a shift from pure $\beta$-$Ga_2O_3$ to pure $\alpha$ -$Ga_2O_3$ at low pressures. Initial results correlating plasma species with phase control will be presented and discussed as a way to overcome the limitations of the low ALD Tg.

6:00pm **VT-WeA12 The Cathodic Arc Plasma from Multi-Element Cathodes**, ***Robert Franz***, Montanuniversität Leoben, Austria

Cathodic arc deposition has been established as one of the standard techniques for the physical vapour deposition of thin films and coatings as it allows the synthesis of a wide variety of materials including metallic films, but also nitrides, carbides and oxides if a reactive background gas is used. In addition, the highly ionised plasma and the achievable high deposition rates allow a variety of control mechanisms to influence the film growth while the manufacturing costs remain rather low due to the short deposition times. With the advent of multifunctional thin films and coatings, the use of multi-element cathodes providing the non-gaseous elements during the synthesis has become an industrial standard. However, a detailed understanding of the discharge properties is vital for the further optimisation of the deposition processes to enable synthesising thin films or coatings with improved properties.

In the present work, the cathodic arc plasma from CrAl and NbAl composite cathodes is studied in detail. The ion energies are measured element, charge state and time resolved in vacuum conditions as well as in the presence of an inert and reactive background gas. Differences in the ion energy and charge state distributions between the plasma from the composite cathodes and corresponding single-element cathodes are noticed. Since it is expected that such differences originate from changes on the cathode surface, namely the formation of intermetallic phases, the erosion behaviour of the cathodes is also analysed. The latter is supported by density functional theory calculations providing additional information about the cohesive energy of the elements which includes the influence of surface texture and temperature. The presence of a background gas generally leads to a reduction of ion energies and charge states. Cathode poisoning effects are mainly observed outside of the main erosion zone. All obtained data are discussed on the basis of correlating the material properties of the cathodes and the plasma properties of the established discharges in order to obtain a comprehensive understanding of the cathodic arc discharge from multi-element cathode and to guide the further development of the deposition of thin films and coatings using such discharges.

## 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.

[1] S. Barja, S. Wickenburg, Z.-F. Liu, Y. Zhang, H. Ryu, M.M. Ugeda, Z. Hussain, Z.-X. Shen, S.-K. Mo, E. Wong, M.B. Salmeron, F. Wang, M.F. Crommie, D.F. Ogletree, J.B. Neaton, A. Weber-Bargioni, *Nat. Phys.* **12**, 751-756 (2016)

[2] Y. Ma, H.C. Diaz, J. Avila, C. Chen, V. Kalappattil, R. Das, M.-H. Phan, T. Čadež, J.M.P. Carmelo, M.C. Asensio, M. Batzill, *Nat. Commun.* **8**, 14231 (2017)

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

[1] S. Nowakowska et al., Nature Communications | 6:6071 | DOI: 10.1038/ncomms7071

[2] J. Lobo Checa et al., Science 325, 17, 300ff (2009)

[3] S. Nowakowska et al, small, 2016; DOI: 10.1002/smll.201600915..

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 $\pi$. 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 $\pi$, 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.

[1] T. G. Pedersen et al., ”Antidot lattices: designed defects and spin qubits”, *Physical Review Letters,* vol. 100, 136804, April 2008

[2] S. S. Gregersen et al., ”Nanostructured graphene for spintronics”, *Phys. Rev. B.* vol 95, 121406(R), March 2017

[3] M. Settnes et al., ”Graphene Nanobubbles as Valley Filters and Beam Splitters”, *Phys. Rev. Lett.* vol. 117, 276801, December 2016

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.

## Applied Surface Science Division
## Room: 13 - Session AS+BI+SA+SS-ThM

### Spectroscopy of the Changing Surface

**Moderators:** Timothy Nunney, Thermo Fisher Scientific, UK, Tony Ohlhausen, Sandia National Laboratory

8:00am **AS+BI+SA+SS-ThM1 In Situ Investigation of the Dynamic Transformations of Model Catalyst Surfaces using Ambient Pressure XPS**, ***Iradwikanari Waluyo****,* Brookhaven National Laboratory **INVITED**

In heterogeneous catalysis, the interaction between reactant molecules and the surface of the catalyst often causes changes in the surface composition and chemical state of the catalyst, which may result in changes in the reactivity of the catalyst. Using ambient pressure x-ray photoelectron spectroscopy (AP-XPS), these changes can be monitored in situ under close-to-realistic conditions. Unlike conventional XPS, which requires UHV conditions, AP-XPS measurements can be performed in the presence of gases at pressures of up to 100 Torr through the use differentially pumped analyzer, small analyzer entrance aperture, and x-ray transparent windows. Although AP-XPS measurements using lab x-ray sources are possible and becoming more common, experiments at modern synchrotron light sources have distinct and significant advantages including tunable photon energy, tightly focused beam, and better resolution. A general overview of the technique as well as recent experimental results will be presented. Examples shown include (1) the potassium-promoted reduction of $Cu_2O$/Cu(111) by CO, in which the reduction of $Cu^+$ to Cu is accelerated by the presence of K through the formation of surface carbonate species, (2) the surface segregation of Pt/Cu(111) model bimetallic catalyst in the presence of various reactant gases, and (3) the reduction of $Cu_2O$/Pt/Cu(111) by $H_2$.

8:40am **AS+BI+SA+SS-ThM3 Observation of Oxygen Binding on PGM-free Electrocatalysts by Ambient Pressure XPS and XAS**, ***Kateryna Artyushkova****,* University of New Mexico*, M.J. Dzara, S. Pylypenko,* Colorado School of Mines*, P. Atanassov,* University of New Mexico

The most promising class of PGM-free materials for oxygen reduction reaction (ORR) is based on graphene-like carbon containing nitrogen and transition metal (MNC). They show promise as replacement of Pt in two different technological platforms - alkaline exchange membrane fuel cells (AEMFCs) and proton exchange membrane fuel cells (PEMFC). It is well established that nitrogen coordination with metal in the carbon network of MNC materials is directly related to ORR activity; however, the ***exact nature of the active sites*** is still debated even after over 50 years of research. Understanding the specific roles of nitrogen and metal in the properties/activity/stability/durability of MNC-based catalytic materials is a prerequisite for the rational design of ORR electrocatalysts with improved performance.

The key component in elucidating the relationship between the chemistry of active sites and activity is a better understanding of the formation of adsorbates, intermediates, and products during reactions occurring within the fuel cell.

*In situ* monitoring reaction steps under realistic conditions in metal-free and metal-containing building blocks will shed light onto the reaction mechanism that is essential for developing active and durable PGM-free catalyst for ORR.

We will report on AP-XPS analysis for series of electrocatalysts belonging to Fe-N-carbon families based on sacrificial support method (SSM) and Metal-organic frameworks (MOF). The effect the nitrogen chemistry and the type of iron have on the oxygen binding was investigated by ambient pressure X-ray Photoelectron Spectroscopy (XPS) and X-ray Adsorption Spectroscopy (XAS) under an $O_2$ environment at operating temperature of the fuel cell. The effect of the relative abundance of different types of nitrogens, such as pyridinic, coordinated to iron and hydrogenated nitrogens (pyrrolic and hydrogenated pyridine) on the preference of oxygen binding is studied by high-resolution nitrogen photoelectron spectra. The role of metallic and atomically dispersed iron will be investigated by a combination of XAS and XPS. Linking differences in oxygen binding to the differences in the chemistry of the electrocatalysts are of ultimate importance for elucidating the oxygen reduction reaction mechanism.

**1**. Artyushkova, K., et al., *Oxygen Binding to Active Sites of Fe–N–C ORR Electrocatalysts Observed by Ambient-Pressure XPS.* The Journal of Physical Chemistry C, 2017. **121**(5): p. 2836-2843.

9:00am **AS+BI+SA+SS-ThM4 In situ Monitoring of Electrochemically Generated Carbene by XPS**, ***Pinar Aydogan Gokturk****, *S.E. Donmez, Y.E. Turkmen, B. Ulgut, S. Suzer*, Bilkent University, Turkey

Ionic liquids provide a platform for fundamental electrochemical studies in vacuum. In this present work, we report an in-situ X-ray photoelectron spectroscopic (XPS) investigation of N-heterocyclic carbene(NHC) generation from the electrochemical reduction of imidazolium based ionic liquids (ILs) through changes in oxidation state of nitrogen atoms. The IL serves as an electroactive material as well as the electrolyte in the cell between a Si substrate which is connected to the instrument ground and a gold wire connected to the sample holder for electrical connection. Through the course of the electrochemical reaction, the positive charge on imidazolium cation is neutralized to give free NHC as reflected by the distinct shifts in the N 1s and C 1s binding energies. The observations are further supported by colorful adduct formation of carbenes with $CS_2$, reversible redox peaks in the voltammogram and the density functional theory calculations. The presented structure and XPS measurements can lead on understanding of the mechanism for various electrochemical reactions.

9:20am **AS+BI+SA+SS-ThM5 The Influence of Water on the Ionic Liquid-Vapor Interface**, ***John Newberg***, University of Delaware, *M.B. Shiflett*, University of Kansas, *A. Broderick, Y. Khalifa*, University of Delaware

Ionic liquids (ILs) have a wide array of applications in biotechnology, coatings, synthesis, separations, and energy sciences. Many of these processes involve either IL-solid or IL-vapor interactions and it is important we understand the fundamental interfacial properties of ILs on a molecular level. Due to the ubiquity of water and the hydrophilic nature of ILs, water can either be unintentionally present or often intentionally added to alter IL properties including density, viscosity, friction and electrochemical window. In this talk we will highlight our recent efforts examining the IL-water vapor interface utilizing ambient pressure X-ray photoelectron spectroscopy (APXPS). APXPS allows for a molecular level assessment of the IL-vapor interface including a quantitative assessment of interfacial water concentration, moiety specific electronic environment changes, structural changes and obtaining adsorbate energetics.

9:40am **AS+BI+SA+SS-ThM6 Ambient Pressure XPS Studies of Model N-C and Fe-N-C Catalysts Under Oxygen Environment**, ***Michael Dzara***, Colorado School of Mines, *K. Artyushkova*, University of New Mexico, *C. Ngo, M.B. Strand, J. Hagen, S. Pylypenko*, Colorado School of Mines

Producing inexpensive polymer electrolyte membrane fuel cells requires significant reduction in the amount of platinum group metal (PGM) oxygen reduction reaction (ORR) catalyst used. High surface area iron- and nitrogen-functionalized carbon (Fe-N-C) materials are a promising PGM-free replacement. These catalysts are very heterogeneous, leading to difficulties in discerning contributions from various potential active sites and identifying the most active species.[1] Techniques such as scanning transmission electron microscopy (STEM), energy dispersive x-ray spectroscopy (EDS), and x-ray photoelectron spectroscopy (XPS) provide structural and chemical information that can be correlated to ORR activity measured with electrochemical methods. Ambient pressure XPS (AP-XPS) and x-ray absorption spectroscopy (XAS) conducted in a humidified $O_2$ environment, at an elevated temperature, and with applied potential offer opportunities to study materials under *in situ* conditions to determine adsorbates, intermediates, and products during ORR steps.[2,3]

In this work, model Fe-N-C catalysts are studied along with reference nitrogen-doped carbon (N-C) materials. Development of model catalyst materials with controlled morphology and speciation can simplify the elucidation of active sites. Micro-porous N-C nanospheres with high graphitic content were synthesized by a solvothermal treatment of resorcinol, formaldehyde, and ethylenediamine, and a subsequent pyrolysis in $N_2$.[4] Incorporation of Fe into the N-C nanospheres was carried out by wet-impregnation of various Fe precursors followed by a second $N_2$ pyrolysis. By varying synthetic parameters, a set of N-C and Fe-N-C nanospheres with diverse compositions and properties were produced. Differences in composition and structure were evaluated using STEM-EDS and XPS, demonstrating control over N and Fe quantity and speciation. Select N-C and Fe-N-C nanospheres were then characterized with *in situ* AP-XPS, and in the case of Fe-N-C nanospheres, *in situ* XAS. By understanding the ORR on these model Fe-N-C nanospheres, synthesis-property-performance conclusions are drawn, guiding the development of highly active Fe-N-C catalysts.

[1] A. Serov, K. Artyushkova, E. Niangar, C. Wang, N. Dale, F. Jaouen, M.-T. Sougrati, Q. Jia, S. Mukerjee, and P. Atanassov, Nano Energy **16**, 293 (2015).

[2] K. Artyushkova, I. Matanovic, B. Halevi, and P. Atanassov, J. Phys. Chem. C **121**, 2836 (2017).

[3] Q. Jia, N. Ramaswamy, H. Hafiz, U. Tylus, S. Strickland, G. Wu, B. Barbiellini, A. Bansil, E.F. Holby, P. Zelenay, and S. Mukerjee, ACS Nano **9**, 12496 (2015).

[4] N.P. Wickramaratne, J. Xu, M. Wang, L. Zhu, L. Dai, and M. Jaroniec, Chem. Mater. **26**, 2820 (2014).

11:00am **AS+BI+SA+SS-ThM10 Real-time Photoelectron Spectroscopy Observation of Oxidation and Reduction Kinetics of Ni(111) Surface**, ***Ryo Taga***, *S. Ogawa, Y. Takakuwa*, Tohoku University, Japan

Nitrogen contained in the air is oxidized and then harmful nitrogen oxide ($NO_X$) is formed in the combustion chamber of engine. Accordingly, the exhaust gas which contains $NO_X$ is purified by catalysts. However, platinum group metals, whose prices are likely to rise by the depletion of resources in the future, are used as the catalysts, so the reduction of the amount used is an important matter for industrial and environmental fields. On the other hand, it has been already known that Ni has an effect to $NO_X$ reduction, but the its catalytic ability disappears when the Ni surface is oxidized. If O atoms on the Ni surface can be efficiently desorbed, Ni is expected as a catalyst for NO reduction. In the previous studies, some of researches have studied about reduction of oxidized Ni surfaces, but the relation between oxide reduction kinetics and behavior of O atoms has not yet been clarified. In this study, the oxidation and reduction kinetics on Ni(111) surfaces was investigated by real-time ultraviolet photoelectron spectroscopy (UPS). to investigate the amount of O atom adsorption and the changes of work function.

The experiments were performed using UPS apparatus with base pressure of $\sim 3\times10^{-8}$ Pa. The Ni(111) surface was firstly cleaned by the $Ar^+$ ion bombardment, and the annealed at 600°C. $O_2$ gas ($1\times10^{-5}$ Pa) was directly introduced to UPS apparatus at the sample temperature of 100°C. After the end of the introduction of $O_2$ gas, the sample heated up to and $H_2$ gas ($1\times10^{-5}$ Pa) was introduced in order to investigate the Ni oxide reduction process. The photoelectron spectra were measured repeatedly each 72 s during oxidation and reduction.

From the time evolution of O 2p photoelectron spectra, we obtained the O 2p uptake curve and the change in work function. When $O_2$ gas was introduced, O 2p intensity increases linearly, so it turned out that the oxidation of Ni(111) surfaces was a zero order reaction. After introduction of $H_2$ gas, O 2p intensity decreases gently for about 500 s and then decreased rapidly. On the other hand, the work function slightly increased and then rapidly decreased. The work function reaches the same value on the clean Ni(111) surface. Therefore, Ni oxide can be reduced completely using $H_2$ gas.

These changes after introduction of $H_2$ gas can be divided into two areas. In the first area, O atoms are drawing from subsurface because of slight increase of work function. In the second area, then, it is suggested that the reduction progresses and the clean Ni surface area enlarges as like to island growth. In the symposium, we will discuss the reduction process of the oxidized Ni surface by NO gas.

11:20am **AS+BI+SA+SS-ThM11 Comparison of Initial Oxidation Kinetics between p- and n-type Si(001) Surfaces Studied by Real-time Photoelectron Spectroscopy**, ***Yuki Sekihata***, *S. Ogawa*, Tohoku University, Japan, *A. Yoshigoe*, JAEA, Japan, *R. Taga*, Tohoku University, Japan, *S. Ishidzuka*, National Institute of Technology, Akita College, Japan, *Y. Takakuwa*, Tohoku University, Japan

An oxidation reaction is the “trade” of electrons between oxygen and other materials, therefore it is thought that there is a difference in the oxidation kinetics on between p-type and n-type Si substrates. In the previous researches about the kinetics of the thermal oxidation of Si, the oxidation rate have not taken account of the difference of conduction type because the thermal oxidation was performed in high temperature region above 600°C named intrinsic region where the intrinsic carrier concentration becomes comparable to the donor or acceptor concentration. On the other hand, oxidation temperature becomes lower to form thin oxide films below 1nm. Therefore, we believe that the difference of conductivity affects an oxidation kinetics on the Si(001) surfaces, but there is no oxidation reaction models that takes into account the difference of conductivity. In this study, we investigated the oxidation reaction kinetics on p- and n-type Si surfaces using real-time ultraviolet photoelectron spectroscopy.

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*** ASSD Student Award Finalist**

The samples for oxidation were p-Si(001) and n-Si(001) surfaces. The dopants were Boron and arsenic for p- and n-type substrates, respectively. Their density of dopants were approximately $10^{18}$ atoms/cm$^3$ so extrinsic region can be kept in the high temperature region even below 700°C. These samples were oxidized using $O_2$ gas at the pressure of $1.0\times10^{-5}$ Pa. During the oxidation reaction, the photoelectron spectra were measured repeatedly, therefore time evolution of the amount of oxygen adsorption, work function, and band bending can be investigated.

In the room temperature oxidation, it is found that oxidation reaction coefficient on n-Si(001) is larger than that on p-Si(001). To clarify the reasons, we focus to the changes of work function due to the formation of dipole layer. The work function of the n-Si(001) surface shows negative value but p-Si(001) is positive value. From this result, we can estimate the adsorption positions of O atoms. O atoms have a negative charge in the bond of Si-O, so it can be assumed that oxygen is placed on the n-Si(001) surfaces, but it is subsurface in case of the p-Si(001) surface. In case of n-Si(001) substrates, the doped electrons spill out into the surface because many electrons exist in the substrate. As the result, oxidation reaction is promoted in the n-Si(001) surface. From these results, we found that there is a difference of oxidation kinetics depending on the conductivity. In the presentation, we will show also the difference of oxide states between them.

11:40am **AS+BI+SA+SS-ThM12 Co-Pyrphyrin on $Cu_2O$(111) and $TiO_2$(110): Properties and Stability under Near Operando Conditions**, ***Zbynek Novotny***, *W.-D. Zabka, M. Hotz, D. Leuenberger*, University of Zurich, Switzerland, *L. Artiglia, F. Orlando, M. Ammann*, Paul Scherrer Institut (PSI), Switzerland, *J. Osterwalder*, University of Zürich, Switzerland

The pyridine-based macrocycle Co-pyrphyrin (Co-Pyr) is a promising molecular water reduction catalyst recently synthesized at the University of Zurich [1]. We investigated $Cu_2O$(111) and $TiO_2$(110) substrates covered with a complete monolayer of Co-Pyr at pressures spanning from ultra-high vacuum (UHV) up to near ambient pressures of 1 mbar of water vapor. To study the surface photovoltage (SPV) effect, samples were illuminated with UV laser light through the electron spectrometer lens system. Both under UHV and water pressures up to 1 mbar, SPV-induced shifts of the order of $\Delta E_k$ = +120 meV were observed in case of $Cu_2O$(111), while for $TiO_2$(110), much smaller SPV shifts of -0.12 meV were observed. X-ray absorption spectroscopy (XAS) of the Co L3-edge in dependence of illumination and water exposure was used to monitor the electronic structure of the Co metal center of Co-Pyr molecules. Comparison to simulated XAS spectra reveals that on the $TiO_2$(110), the Co centers partially transform from a +2 to +1 oxidation state upon exposure to water, while on the $Cu_2O$(111), the Co remains in the +2 oxidation state irrespective of the water exposure. Our measurements provide insights into the stability and behavior of the Co-Pyr molecules studied under near operando conditions, further stimulating the use of these molecular catalysts in the next-generation of solar fuel cells.

[1] Joliat, E et al., *Dalton Transactions* **2016,***45* (4), 1737-1745.

## Biomaterial Interfaces Division
## Room: 12 - Session BI+AS+SA-ThM

## Characterisation of Biological and Biomaterial Surfaces
**Moderators:** Daniel Graham, University of Washington, Tobias Weidner, Aarhus University, Denmark

8:00am **BI+AS+SA-ThM1 Lipid Involvement in the Regenerative Processes of *Dugesia dorotocephala* - A GCIB ToF-SIMS Imaging Study**, ***Tina Angerrer***, *M.J. Taylor, D.J. Graham, L.J. Gamble*, University of Washington

Dugesia dorotocephala are planaria belonging to the class of Turbellaria, or non-parasitic flat worms. They are best known for their fascinating regenerative abilities, which allow them to be cut into more than 200 pieces, each piece missing essential parts necessary for the worms' survival and each re-growing a new flatworm. This level of reorganization involves a complex interplay of a wide range of molecules that varies spatially and temporally but is still poorly understood.

Recently the involvement of peptides and proteins in the process of regrowing the head and developing a new central nervous system has been studied by Sweedler et al.[1] using MALDI imaging. MALDI, in contrast to TOF-SIMS imaging, is capable of studying the distributions of peptides in tissue but spatial resolution is limited and molecules of interest have to be partially predetermined by the choice of matrix.

Using the J105-3D Chemical Imager, (Ionoptika Ltd) equipped with a 40 keV gas cluster ion beam (GCIB), molecules with sizes up to 2000 Da can be localized at a cellular scale, with spatial resolutions better than 3 µm.[2] Since ToF-SIMS is a label free technique, it can be used in an untargeted discovery approach which, in biological samples, is mainly used to study lipid distributions.

Lipids are a diverse group of molecules fulfilling numerous functions such as energy storage and cell signaling, however lipid and fatty acid data for Dugesia in general is very limited and their localizations completely unknown.[3] Our studies were targeted at establishing a full body lipid profile for the different organ systems present in Dugesia as well as monitoring their changes due to stem cell migration during head regrowth and eye/CNS regeneration.

Dugesia flatworms were sectioned on a cryomicrotome at -20 °C and slices were placed on ITO coated glass. After preparation samples were immediately taken to the lab for analysis. Sample preparation and transport time was kept to less than 2 hours to minimize lipid degradation. After SIMS analysis, optical images were acquired in order to facilitate identification of structures seen within the worms. To deal with the increased spectral and spatial complexity provided by our improved instrumental capabilities, imaging PCA was used to "untangle" the data. In this presentation we will present the results of our studies showing the unique lipid distributions throughout Dugesia cross sections and discuss their relevance.

[1] T. H. Ong, *et al.*, J Biol Chem 2016, 291, 8109-8120.

[2] T. B. Angerer, *et al.*, Int J Mass Spectrom 2015, 377, 591-598.

[3] F. Meyer, *et al.*, Biochim Biophys Acta 1970, 210, 257-&.

8:20am **BI+AS+SA-ThM2 Can ToF-SIMS Imaging Explain Biology?**, ***Lara Gamble***, *D.J. Graham*, University of Washington

Imaging time-of-flight mass spectrometry (ToF-SIMS) can provide images of cells and tissues with chemical and molecular specificity. These chemically specific images could revolutionize our understanding of biological processes such as the role of changes in tumor metabolism affecting the response to chemotherapy is under scrutiny. Regions of interest (ROIs) of the tumor can be utilized to compare similar regions from different tissue samples. PCA analysis of ToF-SIMS image data reveals the differences in chemistries between the regions. These results help to identify links between the chemical composition within and around tumors and the changes of these tumors as a response to the treatment. However, often the presentation of ToF-SIMS results might not be in the best format to gain the interest of non-SIMS scientists. Different data processing and data presentation format from clinical trial tissue samples and other tissue samples analyzed with ToF-SIMS will be presented. Additional validation of data interpretation from different techniques will be discussed.

8:40am **BI+AS+SA-ThM3 Applications of XPS for Novel Biomaterial Systems**, ***Jonathan Counsell***, *S.J. Coultas, C.J. Blomfield*, Kratos Analytical Limited, UK, *C. Moffitt*, Kratos Analytical, *S.J. Hutton*, Kratos Analytical Limited, UK **INVITED**

XPS is widely used in the field of biomaterials yielding quantitative elemental and chemical state information [1]. It is possible to identify changes in functional groups present both on the surface and, combined with depth profiling, within the bulk of a biomaterial.

Here we will discuss the latest advancements in XPS as applied to a range of biomaterial systems and examine new possibilities beyond routine spectroscopic analysis. Non-destructive depth profiling of the near surface region is applied to ultra-thin films examining growth modes and film closure mechanisms. With the dual Al/Ag monochromated sources it is possible to vary information depth for relative comparisons on the nature of the uppermost layers. New developments in cluster ion sources now allow soft biomaterials to be depth profiled. Accurate analysis of interfacial chemistry is possible without ion beam damage. XP Imaging will also be discussed for systems exhibiting surface inhomogeneity. Quantitative images yield useful additional information over conventional microscopies. Discussions will concentrate on both model systems and real life applications highlighting the latest possibilities of XPS for this growing field.

[1] Donald R. Miller and Nikolaos A. Peppas, Journal of Macromolecular Science, Part C Vol. 26 , Iss. 1,1986

9:20am **BI+AS+SA-ThM5 Surface Characterization of Polymer Scaffolds: Understanding Surface Modification and Biological Interactions**, ***Michael Taylor***, University of Washington, *M.J. Hawker, M.N. Mann*, Colorado State University, *G.E. Hammer*, University of Washington, *E.R. Fisher*, Colorado State University, *D.J. Graham, L.J. Gamble*, University of Washington

Biopolymers show increasing usage in medical device technologies including joint replacement, stents and tissue engineered supports. (polymer scaffolds). Barriers to successful use of biopolymer usage for medical devices can include ineffective interaction of biological systems with the biopolymer and biofilm formation. Historically, developing medical devices with antibacterial properties have involved inclusion of silver or copper dopants as they facilitate bacterial membrane rupture. Bacterio-static coatings provide an alternative approach by generating a hydrophobic surface that prevents colonisation by reversible adhesion via van der Waals forces prior to anchoring strongly with adhesion structures such as pili. Plasma enhanced chemical vapor deposition (PECVD) is a cheap yet powerful method of introducing chemical functionalities to surfaces as the low temperature high energy process may be used to couple a variety of monomers to biomaterial surfaces. Previous evidence provided by Fisher and coworkers showed that PECVD may be utilised to produce antifouling coatings by modifying polycaprolactone (PCL) with fluorinated organic compounds[1], however the porous morphology of scaffolds required for vascularisation also provides multiple points of attachment for the critical first step in biofilm formation. It is therefore necessary determine the effectiveness of PECVD throughout the scaffold. For this we employ time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) to analyse the surface modification of porous polymer scaffolds.

ToF-SIMS imaging coupled with X-ray photoelectron spectroscopy (XPS) provides a powerful combination of high resolution imaging and elemental quantitative analysis that allows a detailed analysis of the surface. Herein we apply this combination of analysis methods for the determination and quantification of fluorocarbon distribution across a PCL scaffold modified with octafluoropropane by PECVD, determining that a treatment time of 20 minutes Introduces a homogeneous distribution of fluorocarbon film throughout the construct cross section whereas lower treatment times produces a gradient distribution of fluorocarbon, as measured via $CF^+$ and $CF_3^+$ signals

(1) Hawker, M. J.; Pegalajar-jurado, A.; Fisher, E. R. Conformal Encapsulation of Three-Dimensional, Bioresorbable Polymeric Sca Ff Olds Using Plasma-Enhanced Chemical Vapor Deposition. **2014**.

9:40am **BI+AS+SA-ThM6 Seawater Bacteria on Technical Surfaces: Lateral and Vertical Adhesion Forces and Nanomechanical Properties**, *N. Davoudi, K. Huttenlochner,* University of Kaiserslautern, Department of Physics and Research Center Optimas, Germany, *C. Schlegel, M. Huster,* University of Kaiserslautern, Institute of Bioprocess Engineering, Germany, ***Christine Müller-Renno***, University of Kaiserslautern, Department of Physics and Research Center Optimas, Germany, *R. Ulber,* University of Kaiserslautern, Institute of Bioprocess Engineering, Germany, *C. Ziegler*, University of Kaiserslautern, Department of Physics and Research Center Optimas, Germany, Germany

Biofilms are often unwanted, but can also be utilized in biofilm reactors. In such a reactor different forces act on the cells: lateral forces by flow, forces perpendicular to the interface which dominate the first contact and the biofilm formation, and forces on the cell-wall by turgor pressure which influence the viability of the cells. The interplay of these forces plays a major role in the establishment of a biofilm.

Here, we report on the seawater bacterium *Paracoccus seriniphilus* on titanium and glass. Microstructured titanium is our substrate of choice in the reactor. We hence have to understand the influence of wettability, roughness, defined structures, and environmental conditions such as pH and ionic strength on the viability as well as the bacterial attachment and detachment.

In a first set of experiments, the turgor pressure of the bacteria was determined as a function of pH and salinity by measuring force-distance curves with a scanning force microscope (SFM). As a seawater bacterium, *P. seriniphilus* can easily adapt to saline conditions and can survive at NaCl concentrations up to 100 $gL^{-1}$. Depending on the ionic strength the turgor pressure and thus the elasticity and size of the cell changes. *P. seriniphilus* has its optimum pH at 7, but at pH 4 the results point to an active adaption mechanism to acidic conditions. The results at pH 11 show that *P. seriniphilus* cannot adapt to alkaline conditions.

As next step the vertical adhesion forces of a single bacterium were measured as a function of pH, ionic strength, and substrate. The adhesion force of one single cell decreases from pH 4 to pH 9. As a function of the ionic strength, the adhesion forces increase with increasing salt concentration with a pronounced spike (higher adhesion forces) at 0.9 % NaCl. All adhesion force changes completely correlate with the electrostatics as determined by zetapotential measurements. A conditioning film of growth medium strongly decreases the attachment forces. Thus the first bacterial layer should grow without medium at pH 4.

In a last step, the lateral detachment forces of the bacteria were measured. There is a clear correlation between the applied force and the number of moved bacteria, but the detachment forces vary for the individual bacteria. For small lateral forces (0.5 nN), the wettability of the substrate seems to control the detachment process. For higher lateral forces (2-3 nN), the effect of the wettability gets lost and the roughness of the samples controls the cell detachment. These detachment forces are in the same range or higher than the shear forces applied by the fluid flow.

11:00am **BI+AS+SA-ThM10 AVS 2017 Peter Mark Memorial Award Lecture: A Combined Experimental–Simulation Approach for Unraveling Hydrophobic Interactions at the Molecular Scale**, *P. Stock,* MPI for Iron Research, Germany, *J.I. Monroe,* UC Santa Barbara, *T. Utzig,* MPI for Iron Research, Germany, *D.J. Smith, M.S. Shell,* UC Santa Barbara, ***Markus Valtiner****, TU Bergakademie Freiberg, Germany **INVITED**

Interactions between hydrophobic moieties steer ubiquitous processes in aqueous media, including the self-organization of biologic matter. Recent decades have seen tremendous progress in understanding these for macroscopic hydrophobic interfaces. Yet, it is still a challenge to experimentally measure hydrophobic interactions (HIs) at the single-molecule scale and thus to compare with theory.

Here, I will present a combined experimental–simulation approach to directly measure and quantify the sequence dependence and additivity of HIs in peptide systems at the single-molecule scale. We combined dynamic single-molecule force spectroscopy on model peptides with fully atomistic, both equilibrium and nonequilibrium, molecular dynamics (MD) simulations of the same systems. Specifically, we mutate a flexible $(GS)_5$ peptide scaffold with increasing numbers of hydrophobic leucine monomers and measure the peptides' desorption from hydrophobic self-assembled monolayer surfaces. Based on the analysis of nonequilibrium work-trajectories, we measure an interaction free energy that scales linearly with 3.0–3.4 $k_BT$ per leucine. In good agreement, simulations indicate a similar trend with 2.1 $k_BT$ per leucine, while also providing a detailed molecular view into HIs.

Our approach potentially provides a roadmap for directly extracting qualitative and quantitative single-molecule interactions at solid/liquid interfaces in a wide range of fields, including interactions at biointerfaces and adhesive interactions in industrial applications. In this context, I will finally discuss in detail how single molecule unbinding energy landscapes can be utilized to predict scenarios where a large number of molecules simultaneously interact, giving rise to adhesive failure under corrosive and wet conditions.

[1] S. Raman et al. *in Nature Communications***,** 5**(2014)**, 5539.

[2] T. Utzig et al. *in Langmuir*, 31(9) **(2015)**, 2722.

[3] T. Utzig, P. Stock et al. *in Angewandte Intl.***(2016)**.

[4] P. Stock et al. in *ACS Nano***(2017)**, 11 (3), 2586.

11:40am **BI+AS+SA-ThM12 Quantitative Characterization of Bacterial Cells in Solution and on Surfaces**, *C. Sousa, K. Jankowska, L. Parga Basanta, I.M. Pinto,* ***Dmitri Petrovykh***, International Iberian Nanotechnology Laboratory, Portugal

Physicochemical properties of bacterial cells make them challenging subjects for methods typically used to characterize micro- and nanoparticles. Even for conceptually simple parameters, such as size and concentration, direct characterization of live bacteria (and their agglomerates) in solution is far from trivial because bacterial cells are soft and often anisotropic particles with sizes of not more than a few microns. Low contrast, in terms of optical and electronic properties, between bacteria and their aqueous environment complicates any attempted direct measurements in solution. Comparing bacterial cells to non-biological micro- or nanoparticles, whether in the context of mixed samples or calibration measurements, further compounds the complexity of characterizing these systems.

We are using *Staphylococcus aureus* (*S. aureus*) bacteria as a model system for quantitative characterization of bacterial cells. For systematic measurements, *S. aureus* bacteria offer the advantages of nearly spherical shape and of robust viability under a wide range of experimental conditions and treatments. The approximately one micron diameter of live *S. aureus* cells also makes them representative of the sensitivity and resolution challenges encountered in the characterization of bacterial cells. In microscopy, for example, the apparent size of individual *S. aureus* bacteria changes dramatically as they are prepared for measurements with increased spatial resolution: from confocal optical microscopy, to environmental scanning electron microscopy (SEM), to SEM in vacuum.

The objective of our work is to develop and validate a set of complementary techniques that can be used to characterize live bacterial cells. We will describe the use of nanoporous membranes with *S. aureus* suspensions and commonly overlooked effects of centrifugation, mechanical agitation, and other typical sample preparation procedures on the apparent distribution and properties of particles in biological samples. The forced contact of bacteria with these membranes during filtering also suggests their use as model

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* **Peter Mark Memorial Award Winner**

systems for investigating the interactions of bacteria with surfaces having different chemistries and/or morphological features.

12:00pm **BI+AS+SA-ThM13** ***In Situ* Multimodal Imaging of Microbial Communities**, ***Xiao-Ying Yu***, Pacific Northwest National Laboratory

We developed a vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI), to enable direct observations of liquid surfaces and liquid-solid interactions using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and a variety of spectroscopy and microscopy characterization techniques. SALVI was recently applied to investigate biological interfaces in living biofilms and co-cultured microbial communities. In this talk, two case studies will be presented using in situ liquid ToF-SIMS, light microscopy, and fluorescence microscopy. In the first case study, *Shewanella* wild type and mutant were both exposed to environmental stressors such as toxic heavy metal ions (i.e., Cr (VI)) and silver nanoparticles. The response of biofilm and its extracellular polymeric substance (EPS) to the environmental perturbation was investigated using in situ liquid SIMS coupled with structured illumination microscopy (SIM). In the second case, a more complex microbial communities consisting of syntrophic *Geobacter metallireducens* and *Geobacter sulfurreducens* was investigated. Electron donor and electron acceptor in this co-cultured microbial system were characterized first using the more traditional SIMS dry biological sample preparation approach followed by in situ liquid SIMS and confocal laser scanning microscopy (CLSM). The electron transfer between the two species was probed dynamically using the electrochemical SALVI. Correlative imaging is employed to achieve a more holistic view of complexed microbial systems across different space scales. Our results demonstrate that interfacial chemistry involving living microbial systems can be studied from the bottom up based on microfluidics, potentially providing more important understanding in system biology.

## 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$_3$N$_4$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$_2$systems. 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$_3$N$_4$ substrate, mainly because Si$_3$N$_4$ is naturally hydrophobic and bonding has been considered unachievable10. The existing Si$_3$N$_4$ bonding techniques employ high temperature fusion of Si$_3$N$_4$ 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$_3$N$_4$ by activating the surface of Si$_3$N$_4$ using weak HF acid solution. This method can be implemented on Si$_3$N$_4$ 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$_3$N$_4$ 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$_3$N$_4$.

## Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

## Room: 24 - Session HC+SA+SS-ThM

## Mechanisms and Reaction Pathways in Heterogeneously Catalyzed Reactions

**Moderator:** David Payne, Imperial College London

8:00am **HC+SA+SS-ThM1 Effects of Phosphorus and Alkyl Substituents on C-H, C-C, and C-O Bond Rupture within Carboxylic Acids on Ru(0001)**, ***SiWei A. Chang***, *D.W. Flaherty*, University of Illinois at Urbana-Champaign

Transition metal phosphide (TMP) catalysts are selective towards C-O bond rupture during hydrodeoxygenation reactions used to upgrade bio-oil. However, the manner in which bond rupture mechanisms and intrinsic barriers (i.e., C-H, C-C, and C-O bond) differ between transition metals and TMP catalysts are not well understood. In this study, a phosphorus (P) modified Ru(0001) surface is created using sequences of PH$_3$ adsorption and annealing treatments followed by Auger electron spectroscopy to determine the P:Ru ratio. Synthesized P$_{0.4}$-Ru(0001) surfaces have a (r7xr7) low energy electron diffraction pattern and appear to resemble the (111) facet of bulk Ru$_2$P materials. The results from temperature programmed desorption of CO and NH$_3$ demonstrate that the addition of P atoms to Ru(0001) decreases the binding energy of CO and NH$_3$ by ~12 kJ mol$^{-1}$ compared to Ru, suggesting that P atoms decrease the extent of electron exchange between Ru surfaces and adsorbates (i.e., CO and NH$_3$).

Results from temperature programmed reaction (TPR) of C$_1$-C$_4$ carboxylic acid decomposition on Ru(0001) and P$_{0.4}$-Ru(0001) surfaces indicate that both P atoms and the length of alkyl substituents on carboxylic acids (i.e., R = H, CH$_3$, CH$_2$CH$_3$, and CH$_2$CH$_2$CH$_3$) alter the intrinsic activation energy (E$_a$) of bond ruptures. On both surfaces, TPR and reactive molecular beam scattering (RMBS) results are consistent with carboxylic acid decomposition mechanism, that involves the reaction of carboxylate intermediates to form alkyl surface species with either CO (by C-O bond rupture followed by C-

H/C-C bond rupture) or $CO_2$ (by direct C-H/C-C bond rupture). The addition of P atoms to Ru(0001) increases $E_a$ values for the rupture of all bonds (i.e., C-O, C-H and C-C bonds) by 5-50 kJ $mol^{-1}$ and increases also the ratio of CO to $CO_2$ production (in the case of formic acid and acetic acid decomposition). In addition, P atoms weaken the linear correlation that exists between $E_a$ for C-C and C-H bond rupture and the homolytic bond dissociation energies (BDE) of the involved bonds (e.g., R-COOH), thereby decreasing the strength of the correlation from near parity on Ru(0001) (i.e., slope m = 1) to moderate changes with BDE on $P_{0.4}$-Ru(0001) (i.e., slope m = 0.2). The RMBS results from formic acid in the presence of P atoms show a higher production of CO than $CO_2$, which reflects the catalytic consequences of the differences between the C-H and C-O bond rupture energy barriers on $P_{0.40}$-Ru(0001) and those for Ru(0001). Collectively, these results suggest that P atoms alters the production selectivity of CO and $CO_2$ through a greater increase in the energy barriers of C-O bond relative to C-H/C-C bond rupture.

### 8:20am **HC+SA+SS-ThM2 Monitoring Cu(111) Restructuring under Elevated CO Pressures via Polarization Dependent Infrared Spectroscopy**, ***Christopher Kruppe***, *M. Trenary*, University of Illinois at Chicago

Recently it was shown that a Cu(111) surface will reconstruct to form nanoclusters when exposed to 0.1 – 100 Torr of CO.[1] We present the use of polarization dependent – reflection absorption infrared spectroscopy (PD-RAIRS) to monitor the Cu(111) restructuring in real time. Under 10 Torr of CO, PD-RAIR spectra display a peak for CO on top of Cu atoms. Scans were taken periodically and displayed new peaks related to CO bound to the nanoclusters that grow over a period of 30 minutes. Spectra obtained at 10 Torr and 300 K show that the creation of the Cu nanoclusters is correlated with an increase in intensity of these C-O vibrational features, which are only visible due to removal of gas phase CO features from the RAIR spectra. Dissociation of $H_2O$ in UHV occurs on the nanoclusters, which is negligible on unreconstructed Cu(111). Previously the splitting of $H_2O$ was thought to be a geometric effect caused by the nanoclusters as under UHV conditions CO does not adsorb on Cu(111) at room temperature. However, after exposing Cu(111) to 10 Torr of CO at room temperature for 30 minutes strong C-O vibrations are observed upon evacuation of the IR cell. In UHV, the $H_2O$ partial pressure is increased in the IR cell to $2 \times 10^{-8}$ Torr and flowed over the reconstructed Cu(111) crystal. The RAIR spectra indicates there is a reactive CO species that interacts with $H_2O$ to create formaldehyde. This is further confirmed by observing formaldehyde with temperature programmed desorption following $H_2O$ exposure. Auger electron spectroscopy confirms the presence of oxygen on the Cu(111) surface after water exposures in the IR cell. Detailed interpretation of the data requires consideration for the formation of Fe-carbonyls, which can be present in the CO bottle, or produced in the reaction cell. The possibility of Fe as the cause for the CO bound in UHV will be presented.

1. Eren, B.; Zherebetskyy, D.; Patera, L. L.; Wu, C. H.; Bluhm, H.; Africh, C.; Wang, L.-W.; Somorjai, G. A.; Salmeron, M. Activation of Cu(111) Surface by Decomposition into Nanoclusters Driven by CO Adsorption. *Science* **2016**, *351*, 475 LP - 478.

### 8:40am **HC+SA+SS-ThM3 Thermal and Plasma Heterogeneous Catalysis Compared: $CO_2$ and Hydrocarbon Dry Reforming**, *Q. Huang, D.Y. Zhang*, Center of Interface Dynamics for Sustainability, Chengdu, PR China, *E. Schuler, M. Ronda Lloret, G. Rothenberg, N.R. Shiju,* van 't Hoff Institute for Molecular Sciences, Amsterdam, The Netherlands, ***Aart Kleyn***, Center of Interface Dynamics for Sustainability, PR China **INVITED**

Endothermic catalytic reactions require operation at elevated temperatures. The heating required is usually obtained by combustion of hydrocarbons and contributes to $CO_2$ emission. Instead electricity obtained in a sustainable should drive the reaction. In addition, it is desirable that the energy transfer involved is done in a bond specific manner. Plasma excitation and dissociation of molecules can serve this purpose. In plasma, all molecular degrees of freedom are not in equilibrium and dissociation of $CO_2$ can be realized much more efficiently than in thermodynamic equilibrium. There is a preferential vibrational excitation of $CO_2$.

In Chengdu we use a plasma chemical reactor with mass spectroscopy, infrared spectroscopy, optical emission spectroscopy and a Langmuir probe to study the characteristics of the plasma, reaction products and the catalyst. In Amsterdam we use a thermal reactor and gas chromatography to study reaction products. The reactions are carried out at pressures of several hundreds of Pa up to atmospheric in Ar buffergas. Catalysts are prepared in the usual way.

The simplest reaction studied in the plasma reactor is the dissociation of $CO_2$ into CO and $O_2$. We find energy efficiencies higher than 45%, indicating that the system is not in thermodynamic equilibrium and plasma favors vibrational excitation to translational heating. Adding a catalyst like AgO or NiO on $Al_2O_3$ does not enhance the yield. However, a purely metallic catalyst does significantly enhance the yield.

Optical emission spectroscopy shows that the radiofrequency (RF) and microwave (MW) plasma behave quite different. In the MW plasma predominantly emission from the $C_2$ Swann-band is seen, whereas the RF plasma shows mainly chemiluminescence from excited CO. This is due to a different electron excitation mechanism.

In the case of dry reforming of $CH_4$ with $CO_2$ in the plasma reactor we find that addition of an oxidic catalyst does not enhance the yield of CO + $H_2$. In the case of dry reforming of butane ($C_4H_{10}$) to yield butene ($C_4H_8$), plasma reforming with or without catalyst does shows only small conversion. Mainly cracking of butane into $C_2H_x$ is seen and polymerization. However, running the same reaction under high temperature conditions in a thermal reactor yields a satisfactory conversion. A Co based catalyst has the best performance.

These studies allow us to obtain mechanistic information on the conversion of simple molecules, pretreated by plasma, on various catalysts. We are exploring to what extend direct Eley-Rideal reactions are relevant in the plasma reactor. This reaction mechanism is very unlikely under thermal conditions.

### 9:20am **HC+SA+SS-ThM5 Imaging the Molecular Origins of Symmetry Breaking on Well-defined Surfaces**, ***Amanda Larson***, *R.T. Hannagan, E.C.H. Sykes*, Tufts University

Understanding the interaction of prochiral reactants with chiral modifiers on surfaces is a key step towards controlling heterogeneous enantioselective catalysis. We have chosen a simple model system composed of interacting chiral propylene oxide and propene molecules on a Cu(111) surface that is amenable to both scanning probe and desorption studies. Low temperature scanning tunneling microscopy (STM) enables an unprecedented level of spatial resolution of the enantioselective molecule-molecule interactions and their dynamics. STM imaging of propylene oxide and propene molecules at 5 K reveals that both molecules, when in isolation on the surface, behave as molecular rotors. Furthermore, the chirality of individual propylene oxide molecules can be discerned from the STM images of the rotating molecule. While propene is achiral in the gas phase it become chiral when bound to surfaces and STM also allows us to distinguish between its surface-bound enantiomers. When studied separately, repulsive forces between both sets of molecules disperse them on the surface at low coverages. However, when co-dosed we observe an attraction between propylene oxide and propene and they form complexes in which their rotation is inhibited. Temperature programmed desorption measurements are used to quantify these chiral modifier-molecule interaction strengths. Finally, the geometry of individual propene and propylene oxide molecules can be determined within the complexes and 1:1 chiral interactions deciphered.

### 11:00am **HC+SA+SS-ThM10 A Surface Science Approach for New Heterogeneous Catalyst**, ***Ib Chorkendorff***, Technical University of Denmark **INVITED**

First, we shall discuss how surface science and mass-selected nanoparticles can be used to make efficient model systems for heterogeneous catalysts. We shall demonstrate how mass-selected nanoparticles of CuZn alloys can be used to elucidate the dynamics of the methanol synthesis catalysts. The produced nanoparticles will be compared to the conventional CuZnAl at 1 bar for synthesizing methanol from $CO_2$ and $H_2$ [1, 2, 3]. The methanol synthesis on CuZn will also be discussed with respect to our recent findings of using alloys of NiGa for methanol synthesis [4]. The use of mass-selected nanoparticles will be further demonstrated for electrochemical Oxygen Reduction Reaction, which is really the limiting reaction in Proton Exchange Membrane Fuel Cells. Here we have found entirely new classes of electro-catalysts by alloying Pt with early transition metals [5] or the lanthanides [6]. We have also shown that it is possible to make mass-selected nanoparticles of these alloys with very good activities [7] and PtGd alloys [8]. Finally, we shall also discuss how planar surface science can be used to identify new catalysts for ammonia oxidation. We shall demonstrate how Copper deposited on Ruthenium can enhance the activity substantially and give rational explanations for this enhancement which also can be transferred to high area catalysts used for diesel exhaust treatment [9].

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11:40am **HC+SA+SS-ThM12 Chemisorption and Oxidation of $H_2$ on $IrO_2(110)$**, ***Tao Li***, *Z. Liang,* University of Florida, Gainesville*, M. Kim, A. Asthagiri,* The Ohio State University*, J.F. Weaver,* University of Florida, Gainesville

Understanding the interactions of hydrogen with $IrO_2$ surfaces is central to improving applications of electrocatalysis as well as exploiting the high-reactivity of $IrO_2$ for promoting methane activation. In this talk, I will discuss our recent investigations of the dissociative chemisorption and oxidation of $H_2$ on stoichiometric and oxygen-rich $IrO_2(110)$ surfaces. We find that $H_2$ dissociation is highly facile on s-$IrO_2(110)$, with more than 90% of a saturated $H_2$ layer dissociating below 225 K during temperature-programmed reaction spectroscopy (TPRS). We observe only $H_2O$ desorption in a broad TPRS peak from about 400 to 780 K after generating low $H_2$ coverages on s-$IrO_2(110)$ at about 90 K. At high $H_2$ coverages, we also observe small $H_2$ desorption peaks at 200 and 530 K which we attribute to molecular and recombinative desorption processes, respectively. We present evidence that $H_2$ dissociation on $IrO_2(110)$ occurs through a mechanism wherein $H_2$ σ-complexes adsorbed on the coordinatively-unsaturated (cus) Ir atoms serve as precursors for $H_2$ dissociation. We show that oxygen atoms adsorbed on the cus-Ir sites, so-called on-top O-atoms, hinder $H_2$ dissociation on $IrO_2(110)$, while also facilitating $H_2O$ desorption and promoting H-atom transfer from bridging O-atoms to on-top O-atoms. I will also discuss the results of density functional theory calculations of $H_2$ dissociation and initial steps of $H_2O$ formation on stoichiometric and O-rich $IrO_2(110)$.

## Advanced Ion Microscopy Focus Topic
## Room: 7 & 8 - Session HI+BI+NS+TR-ThM

## Advanced Ion Microscopy Applications
**Moderators:** Armin Golzhauser, Bielefeld University, Germany, Olga Ovchinikova, Oak Ridge National Laboratory

8:00am **HI+BI+NS+TR-ThM1 Scanning Helium Atom Microscopy: Imaging with a Deft Touch**, ***Paul Dastoor***, University of Newcastle, Australia **INVITED**

Delicate structures (such as biological samples, organic films for polymer electronics and adsorbate layers) suffer degradation under the energetic probes of traditional microscopies. Furthermore, the charged nature of these probes presents difficulties when imaging with electric or magnetic fields, or for insulating materials where the addition of a conductive coating is not desirable. Scanning helium microscopy is able to image such structures completely non-destructively by taking advantage of a neutral helium beam as a chemically, electrically, and magnetically inert probe of the sample surface. Here, we present scanning helium micrographs demonstrating image contrast arising from a range of mechanisms including, for the first time, chemical contrast observed from a series of metal-semiconductor interfaces [1]. The ability of neutral helium microscopy to distinguish between materials without the risk of damage makes it ideal for investigating a wide range of systems.

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8:40am **HI+BI+NS+TR-ThM3 Biofilm Structure of Geobacter Sulfurreducens by Helium Ion Microscopy**, ***Alex Belianinov***, Oak Ridge National Laboratory*, M. Halsted, M.J. Burch,* Oak Ridge National Laboratory*, S. Kim, S. Retterer,* Oak Ridge National Laboratory

Microbial communities form biofilms on material surfaces in a multitude of ecosystems, from the root hairs of a plant to the human gut. The hallmarks of an established biofilm include (1) the attachment of microbial cells to a surface, (2) production of extracellular polymeric substance, (EPS) (3) a complex structure or "architecture," and (4) the ability to exchange genetic information between cells. [1] Geobacter sulfurreducens forms unique, electrically conductive biofilms, a property that can be exploited in production and design of microbial fuel cells. In this work, examine biofilm formation, and biofilm properties of Geobacter sulfurreducens using a Scanning Electron Microscope (SEM) as well as a Helium Ion Microscope (HIM).

SEM is a high-resolution imaging technique used for characterization of a broad variety of materials. However, in order to image highly insulating, soft biological materials, the samples must be coated for charge compensation. These (typically) metallic coatings create a homogenous surface and may cloak true biological behavior and material contrast in the micrograph. In the case of Geobacter sulfurreducens, metal coating precludes detailed investigation of microbial attachment, presence of EPS, and fine surface details that may elucidate the mechanisms behind architecture formation and genetic material exchange.

Recently introduced HIM, offers more flexibility in investigating biological samples, as highly insulating sample can be imaged sui generis, without the use of a conductive coating. [2] This opens new pathways to capturing high resolution spatial details of biofilm formation and biofilm properties. Furthermore, high-resolution HIM imaging reveals true surface details of Geobacter sulfurreducens, such as flagella or pilin typically inaccessible by SEM. Finally, the effects of different sample preparation strategies for SEM and HIM will be illustrated and discussed.

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Acknowledgements:

This research was supported by Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

9:00am **HI+BI+NS+TR-ThM4 Channeling via Transmission He Ion Microscopy**, ***Christoph Herrmann***, Simon Fraser University, Canada*, S.A. Scott, M. Lagally,* University of Wisconsin-Madison*, K. Kavanagh,* Simon Fraser University, Canada

The spatial coherence of focussed helium (He) ion beams is significant. The He ion source is atomic size (W filament tip) and the resolution from scanning probe, ion-induced secondary electron images is sub 1 nm. Scanning transmission images with atomic resolution are theoretically predicted. We have been experimenting with a digital camera located underneath the sample stage and tilt cradle of our instrument (Zeiss Nanofab). The camera consists of an array of Si p-i-n diodes (55 μm square pixels) that allow direct detection of single He ions and atoms (20 keV - 40 keV). We have previously reported that the beam intensity profiles are uniformly distributed, as expected from the small de Broglie wavelength (80 fm), with a half angle convergence of 2 mrad.[1] At beam currents in the pA range the detector count rate was consistent with one count per He ion or atom. In this talk, we will present results that indicate planar channeling in single crystalline Si (100) membranes (25 nm - 75 nm thick). The transmission intensity as a function of position depends on the beam incidence angle, and beam energy, with random incidence profiles consistent with monte carlo scattering and range calculations (SRIM). The peak in transmission as a function of incidence angle has a half angle width of 1° at 25 kV. These results will be compared with theoretical calculations based on impact factors at low energies. Channeling experiments with other thin crystalline materials including graphite and MgO will be discussed. **Acknowledgements**: We thank Norcada Inc. (Edmonton) for supplying Si (100) 50 nm thick membranes; NSERC, CFI/BCKDF, 4DLABs for funding. [1] K.L. Kavanagh and C. Herrmann, Direct He Detection for Transmission Helium Ion Microscopy, Microsc. Microanal. submitted 2017.

9:20am **HI+BI+NS+TR-ThM5 Rapid Imaging of Nano-Porous Catalyst Particles Via Helium Ion Microscopy**, *M.J. Burch, A.V. Ievlev,* ***Holland Hysmith***, Oak Ridge National Laboratory*, K. Mahady, P.D. Rack,* University of Tennessee*, L. Luo,* ExxonMobil Chemical Company*, A. Belianinov,* Oak Ridge National Laboratory*, S. Yakovlev,* ExxonMobil Chemical Company*, O.S. Ovchinikova,* Oak Ridge National Laboratory

Porous materials are some of the most important modern day material systems, as the pore structure defines many materials applications and functionality. The pore structure of catalyst precursor particles, in particular, is of great importance to the catalyst community, as this pore structure dictates the efficiency and efficacy of grown polymers. However, despite the importance of these materials systems, there are few techniques to analyze pore size and structure. The most common technique is gas absorption, where the amount of gas absorbed and desorbed from a known amount of material is tracked and the average pore volume and size can be extracted. However, the technique is heavily dependent on sample quality and which fitting model is used to calculate volume and size. In addition, the technique is quite slow, where generally at most a single sample can be analyzed a day.

In this work, we demonstrate a novel technique to directly image and quantify pore size in nano-porous catalyst precursor particles via helium ion microscopy. We demonstrate the technique by directly imaging the surface pore structure of $SiO_2$ precursor catalyst particles with helium ion microscopy. Using modern day data analytics, we created an automated routine to extract pore size and distributions. We show that our HIM based technique shows comparable data to the industry standard gas absorption technique, within a 5 percent difference between the techniques of a known porous samples.

Further, to determine the effect of the helium beam on the surface of the $SiO_2$ particles, we simulate the beam interaction between porous $SiO_2$ particles and the helium beam. At low ion doses the surface modification by the ion beam is quite negligible, where at higher ion doses, significant surface modification is observed.

In conclusion, we've demonstrated a novel technique to directly visualize and quantify nano-pore size and structure in $SiO_2$ that yields complimentary data to gas absorption.

**Acknowledgements**

This work was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility. The users acknowledge the ExxonMobil Chemical Company for funding.

### 9:40am **HI+BI+NS+TR-ThM6 Ion Beam Induced Current Measurements of Solar Cells with Helium Ion Microscopy**, *A. Belianinov, S. Kim,* ***Ryan Cannon****, M.J. Burch, S. Jesse, O.S. Ovchinnikova*, Oak Ridge National Laboratory

The scanning electron microscope (SEM) is a versatile high-resolution microscopy tool, and perhaps the most widely used imaging platform across many engineering and scientific fields [1]. Within the last decade, another microscopy technique based on a gaseous field ionization source, utilizing Helium and Neon ions has been introduced [2]. While the popularity of the SEM is hardly challenged by the Helium Ion Microscopy (HIM), there are instances when imaging with ions offers significant advantage as opposed to imaging with electrons. In principle, both HIM and the SEM share many similarities, for example, a HIM operating at 40 keV will generate ions with velocity comparable to SEM operating at 5 keV. However, due to much higher stopping power of ions, as compared to electrons, ion based secondary electron (iSE) will be higher. Also, as a result, there is little ion backscattering, and consequently, the concentration of the ion-generated iSE2 (additional secondary electron generated by SE interaction within the material) is usually insignificant.

In this work, we exploit small interaction volumes in the HIM, and take advantage of the lower iSE2 yield, and positively charged helium ions to map ion beam induced current (IBIC) in solar cell materials. Similar studies, using electrons, have visualized induced current profiles at grain profiles in polycrystalline solar cells, and in silicon [3, 4]. Furthermore, broad ion sources have been utilized in conjunction with scanning probe systems in the past to map out current changes in FinFETs [5]. We are interested in utilizing the HIM to map current at the nanoscale near p-n junctions in CdTe to elucidate differences in contrast captured by the ion beam induced current, as opposed to the electron beam induced current. These findings will illustrate the peculiarities of ionic transport in these solar cell materials, and will evaluate the HIM technology as a potential quality control tool.

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### 11:00am **HI+BI+NS+TR-ThM10 Writing Magnetic Domains with a Helium Ion Microscope**, ***Daniel Emmrich***, Bielefeld University, Germany, *A. Gaul, D. Holzinger, A. Ehresmann,* University of Kassel, Germany, *F. Karimian, M. Klug, J. McCord,* Kiel University, Germany*, A. Beyer, A. Gölzhäuser*, Bielefeld University, Germany

Microscopes based on gas field ion sources offer surface-sensitive, high resolution imaging and state of the art nano-machining.[1] It was further shown that light ions like helium or neon enable a modification of the magnetic properties, e.g., turning thin films from paramagnetic to ferromagnetic state, without significant sputtering.[2]

In this work, two-dimensional ion bombardment induced magnetic patterning (IBMP)[3] is demonstrated with a helium ion microscope to create magnetic domains in an exchange biased thin film system. Such a system consists of a thin ferromagnetic layer coupled to an underlying antiferromagnet. Low dose helium ion irradiation at an energy of 15 keV in an external magnetic field leads to a new, remanent magnetization direction, determined by the external magnetic field. By subsequently patterning the sample in differently orientated external magnetic fields, complex magnetic domain patterns such as chiral structures can be written. Based on magnetic force microscopy and optical Kerr microscopy, we will discuss the achievable resolution as well as the shapes of different artificial magnetic domains.

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### 11:20am **HI+BI+NS+TR-ThM11 Characterisation of Nanomaterials on the Helium Ion Microscope using Correlative Secondary Electron and Mass Filtered Secondary Ion Imaging**, *J.-N. Audinot, D.M.F. Dowsett, F. Vollnhals, T. Wirtz,* Luxembourg Institute of Science and Technology (LIST), Luxembourg, ***John A. Notte***, Carl Zeiss Microscopy, LLC

In order to add nano-analytical capabilities to the Helium Ion Microscope, we have developed a Secondary Ion Mass Spectrometry (SIMS) system specifically designed for the Zeiss ORION NanoFab [1-3]. SIMS is based on the generation and identification of characteristic secondary ions by irradiation with a primary ion beam (in this case helium or neon). It 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 SIMS, the typical interaction volume between the impinging ion beam and the sample is around 10 nm in the lateral direction. As the probe size in the HIM is substantially smaller (both for He and Ne), the lateral resolution on the integrated HIM-SIMS is limited only by fundamental considerations and not, as is currently the case on commercial SIMS instruments, the probe size [4,5]. We have demonstrated that our instrument is capable of producing elemental SIMS maps with lateral resolutions down to 12 nm [3-5].

Furthermore, HIM-SIMS opens the way for in-situ correlative imaging combining high resolution SE images with elemental and isotopic ratio maps from SIMS [4,5]. This approach allows SE images of exactly the same zone analysed with SIMS to be acquired easily and rapidly, followed by a fusion between the SE and SIMS data sets.

In this talk, we will present a number of examples taken from various fields of materials science (battery materials, solar cells, micro-electronics, coatings) and life science (nanoparticles in creams and biological tissues) to show the powerful correlative microscopy possibilities enabled by the integrated HIM-SIMS instrument.

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## Manufacturing Science and Technology Group
## Room: 5 & 6 - Session MS-ThM

## Additive and Other Novel Manufacturing Techniques
## Moderator: Vincent Smentkowski, General Electric Global Research Center

8:00am **MS-ThM1 Thermal Spray for Additive Manufacturing**, *A. Agarwal,* ***Cheng Zhang***, Florida International University **INVITED**

Additive manufacturing is gaining popularity in the commercial domain due to engineering and economic advantages over conventional manufacturing, such as reduced material wastage, lightweight components, and rapid manufacturing to near net shapes. Thermal spray processes are promising for additive manufacturing of metals, ceramics as well as polymers. Thermal spray is a wide range of manufacturing processes in which material in the form of particles/wire is sprayed and deposited at elevated temperatures to form coatings and free-standing 3D structures. These processes include plasma spray, flame spray, detonation gun, high-velocity oxyfuel spray, wire arc spray and cold gas spray. Thermal spray allows rapid processing of near net shape structures at bulk scale with complex shapes, contours, and variable thickness. Thermal spray techniques enable manufacturing of composite materials and functional gradient structures. While thermal sprayed coatings have diverse applications in wear resistance, biomedical implants, thermal barrier, corrosion protection, direct write sensors, fuel cells, etc., free-standing 3D structures fabricated by thermal spray are not as extensively used. This talk will present an overview of the state of the art of additive manufacturing via thermal spray techniques. The challenges and potential solutions will be described. A Novel in situ characterization techniques will be discussed that provide insight into processing-structure-property correlations in bulk 3D components fabricated by thermal spray. This will enable development of bulk components with predictable properties by thermal spray techniques.

8:40am **MS-ThM3 Eliminating Excess Flow during Active Brazing through Surface Preparation with ALD**, ***Ronald Goeke***, *C.A. Walker, P. Sarobol, P.T. Vianco*, Sandia National Laboratories

Active brazing is a permanent metallurgical joining method in which highly reactive brazing filler metals are utilized to directly braze metals to nonmetals. Due to limitations of the active brazing filler metal spreading adequately over a nonmetal surface, the filler metal must be preplaced between the two faying surfaces of the brazement. When heated the liquid filler metal is normally contained within the brazement by capillary attraction. Chemical reactions at the brazement faying surfaces often lead to excessive braze filler metal flow, rendering the brazed assembly useless. Conformal coatings nanometers thick, deposited by atomic layer deposition (ALD) onto the metal surfaces, modify the surface chemistry to eliminate excessive filler metal flow. Unlike other means used to prevent excessive filler metal flow, the thin ALD coating does not hinder next assembly processes, does not require post-braze cleaning or alter the base material mechanical properties.

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9:00am **MS-ThM4 Analysis of Textile Surface Characteristics for Direct Write Printing of Ink-based Textile Electronics**, ***Jesse Jur***, *R. Bhakta, H. Shahariar, H. Soewardiman*, North Carolina State University

Direct write printing is studied as a method for producing large-area electronics directly onto flexible textile substrates. This process delivers viscous conductive particle inks in the range of 1 - 20 kilo-cps to a surface via a pressure-backed nozzle, making it a process that has key similarities and differences to traditional screen-printing and ink-jet printing. In this work, key correlations are defined between the print head speed and viscosity on the ability to design electronic device structures on textile substrates. For standard surface printing on the textile, sheet resistance values ranges from 5 - 16 mOhms/sq for Ag and Ag/AgCl inks. In addition, the ability to design devices through the bulk of the textile is explored. Ink penetration is shown to vary between to 100 microns into the textile structure based on the hydrophobic characteristic of the textile substrate, ink viscosity and the delivery pressure of the ink. Such penetration is shown to fabricate multi-layered printed structures on the surface and back of the textile. Device applications range from printed/flexible heaters, antennas, circuit boards, and dry electrodes for biopotential monitoring.

9:20am **MS-ThM5 Three-Dimensional Silicon Mesostructures for Bioelectric Interfaces**, ***Yuanwen Jiang****, *B. Tian*, The University of Chicago

Silicon-based materials exhibit biocompatibility, biodegradability as well as a spectrum of important electrical, optical, thermal and mechanical properties, leading to their potential applications in biophysical or biomedical research. However, existing forms of silicon (Si) materials have been primarily focused on one-dimensional (1D) nanowires and two-dimensional (2D) membranes. Si with three-dimensional (3D) mesoscale features has been an emerging class of materials with potentially unique physical properties. Here, we incorporated new design elements in the traditional chemical vapor deposition (CVD) method to prepare various forms of 3D Si mesostructures and studied their functional biointerfaces with cellular components. In the first example, an anisotropic Si mesostructure, fabricated from atomic gold-enabled 3D lithography, displayed enhanced mesoscale interfacial interactions with extracellular matrix network. This topographically-enabled adhesive biointerface could be exploited for building tight junctions between bioelectronics devices and biological tissues. Another Si mesostructure with multi-scale structural and chemical heterogeneities, was adopted to establish a remotely-controlled lipid-supported bioelectric interface. We further adapted the bioelectric interface into the non-genetic optical modulation of single dorsal root ganglia neuron electrophysiology dynamics. Our results suggest that the dimensional extension of existing forms of Si could open up new opportunities in the research of biomaterials manufacturing and application.

9:40am **MS-ThM6 Microplasma Sputtering for 3D Printing of Metallic Microstructures**, ***Yosef Kornbluth***, Massachusetts Institute of Technology, *R. Matthews, L. Parameswaran, L. Racz,* MIT Lincoln Laboratory, *L. Velásquez-García*, Massachusetts Institute of Technology

Additive manufacturing technologies promise to transform the development and production of agile microsystems, but are limited by the ability to print microelectronics-quality interconnects. State of the art 3D printing techniques for conductors cannot yet deliver the feature resolution and electrical conductivity required for high performance microcircuits, and have materials and substrate constraints and post-processing requirements. We develop a novel microplasma sputtering system that has the potential to provide direct-write capability of quality metal interconnects on non-standard substrates for integrated circuits, with future extensibility to dielectrics and semiconductors. The microplasma is generated at atmospheric pressure, obviating the need for a vacuum. By manipulating the metal at the atomic level, we retain the resistivity of bulk metal, and by sputtering the metal, we eliminate the need for post-processing or lithographic patterning.

We have modeled and constructed a first-generation system that incorporates continuous material feed and focusing with electrostatic fields. The microplasma head has a grounded central target wire, surrounded by two pairs of electrodes evenly distributed around the target: two opposing electrodes biased at a positive voltage to form the plasma, and two biased at a negative voltage to focus the plasma. Electrostatic fields guide the ionized fraction of the working gas towards a localized spot on the substrate. The directed ions collide with other gas atoms and, crucially, with sputtered metal atoms from the target. The net force of these collisions drags the metal atoms towards the substrate. This indirect electrostatic focusing mitigates the inherent spread of the sputtered material caused by collisions at atmospheric pressure, and enables fine feature definition. By focusing the sputtered material, we achieve imprints significantly narrower than the cathode, avoiding the need to machine target electrodes as small as the desired feature size.

Multi-physics COMSOL simulations predict that features orders of magnitude narrower than the target-wire cross section can be printed if the electric fields are set appropriately. We present findings from our COMSOL simulations and experimental confirmation of key findings.

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* **National Student Award Finalist**

# 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 $\mu m^2$ 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.

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## Plasma Science and Technology Division
## Room: 23 - Session PS+NS+SS+TF-ThM

### Atomic Layer Etching I
**Moderators:** Andrew Gibson, University of York, UK, Saravanapriyan Sriraman, Lam Research Corporation

8:00am **PS+NS+SS+TF-ThM1 Strategies to Control the Etch per Cycle During Atomic Layer Etching of $SiO_2$ and $SiN_x$**, ***Ryan Gasvoda***, Colorado School of Mines, *S. Wang, E.A. Hudson,* Lam Research Corporation, *S. Agarwal,* Colorado School of Mines

Decreasing device dimensions and the incorporation of increasingly complex 3D architectures place new constraints on conventional plasma processing techniques. One method to address the limitations of conventional etching is atomic layer etching (ALE) which can provide low damage and atomic-scale etch control. ALE has been extensively studied for a variety of materials, including $Al_2O_3$, $HfO_2$, Si, and Si-based dielectrics. In this study, we have explored the atomistic-level details of an $SiO_2$ and $SiN_x$ ALE process consisting of a hydrocarbon-containing precursor dose, $CF_x$ deposition from a $C_4F_8$/Ar plasma, and an Ar plasma activation step in which the $CF_x$ film is activated and the underlying substrates are etched. In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and *in situ* four-wavelength ellipsometry during ALE to monitor the surface reactions and film composition as well as the net film thickness during the deposition and etching steps.

Sequential cycles of ALE of $SiO_2$ show a drift in the etch per cycle (EPC) with increasing cycle number. We attribute the drift in EPC is from excess $CF_x$ that is liberated from the reactor walls in the Ar plasma step. This increase in the EPC occurs even though the infrared spectra confirm that the $CF_x$ deposition onto the $SiO_2$ film is reproducible from cycle to cycle. To minimize the drift in EPC, Ar plasma half-cycles of twice the length are employed, which allows for the removal of $CF_x$ from the reactor walls during each cycle, thus creating more reproducible chamber wall conditions.

To further control the EPC, a hydrocarbon precursor prior to the start of ALE retards the EPC. A broad feature centered at ~1,400 $cm^{-1}$ builds up on the surface with increasing hydrocarbon dose frequency and cycle number, which is assigned to a carbonaceous film of $CH_xF_y$. The film acts as a blocking layer which prevents the activation of $CF_x$ at the $CF_x/SiO_2$ interface and thus limits $SiO_2$ etching. No graphitic carbon buildup is observed. However, increasing the Ar plasma half-cycle length limits the buildup of the $CH_xF_y$ film and increases the EPC. Using the same baseline processing conditions as ALE of $SiO_2$, ALE of $SiN_x$ leads to a carbonaceous film buildup of both $CH_xF_y$ and nitrile species at ~2,225 $cm^{-1}$ which accumulates over cycle number and eventually leads to an etch stop. A longer Ar plasma half-cycle limits the accumulation of the $CH_xF_y$ film and the EPC drift. The addition of a hydrocarbon precursor retards the EPC in a similar fashion as observed on the $SiO_2$ film.

8:20am **PS+NS+SS+TF-ThM2 Enabling Atomic Layer Etching of Magnetic and Noble Metal Alloys**, ***Nicholas Altieri****, *E. Chen*, University of California, Los Angeles, *J.K. Chen*, Lam Research Corporation, *J.P. Chang*, University of California, Los Angeles

Etching of magnetic and noble metals alloys utilized in ferromagnetic thin films crucial to the operation of magnetic memory has created a processing bottleneck, due to their chemically resistant nature. Widely-used etch techniques, including noble ion sputtering, exhibit limited success at patterning high aspect ratio features as well as a lack of selectivity. Furthermore, as feature sizes shrink, the demand for atomic level precision in patterning increases. A generalized strategy has been developed to enable dry etch processes shown to be effective for patterning elemental and alloyed metal thin films through the use of surface modification. Controlling the thickness of the modified layer allowed for direct control of the amount of material removed, indicating that this process would be viable for achieving atomic layer etch.

The etch of Co and Pt, elements commonly used in the magnetic memory stack, as well as ferromagnetic alloys CoPt and $Co_{30}Fe_{45}B_{25}$ were studied in this work. Inductively coupled oxygen plasma was utilized for surface modification, and organics including oxalic acid, formic acid, acetylacetone, and hexafluoroacetylacetone were investigated as chemical etchants.

Pt, Co, CoPt, and CoFeB thin films were first studied using continuous exposure to organic solutions. Pt showed no etch beyond the removal of a thin layer of native oxide. CoPt and CoFeB were shown to etch at rates up to 10 nm/min in formic acid solutions without plasma modification. Upon translation to the gas phase, where the concentration of organics was substantially lower, no etch was observed across all materials when continuously exposed to organic acid vapor.

Plasma oxidation was then utilized to chemically modify the surface through generation of directional metal-oxide bonding prior to treatment with organics. Subsequent exposure to formic acid solution indicated preferential and complete removal of metal oxides. A dual-step dry etch process consisting of plasma oxidation and organic vapor dosing was then developed which exhibited etch rates of 0.5, 2.8, 1.1, and 1.8 nm/cycle for Pt, Co, CoPt and CoFeB, respectively, and removing metallic oxides.

In formic acid solution, $PtO_2$ exhibited infinite selectivity to Pt, while oxidized CoPt and CoFeB were observed to have selectivities of 6.4 and 3.1, respectively, compared to their unoxidized counterparts. In the vapor phase, each oxidized material exhibited nearly infinite selectivity to each corresponding metallic film. Coercivity values ($H_c$) of 20 and 3.5 Oe were measured for Co and CoFeB before processing conserved to up to 99% of their original pre-processing values.

8:40am **PS+NS+SS+TF-ThM3 Directional Atomic Layer Etching: First Principles, Modelling and Applications**, ***Thorsten Lill***, *K. Kanarik, I.L. Berry, S. Tan, Y. Pan, V. Vahedi, R.A. Gottscho*, Lam Research Corporation **INVITED**

Atomic layer etching (ALE) has recently been introduced into manufacturing to produce 10 nm logic devices. ALE is an etching technology that deploys time or space separated and self-limited steps. In directional ALE, at least one of the two steps has to be directional, i.e., has to transfer momentum to the surface and/or be sensitive to line of sight. Ion bombardment is most commonly used to realize directional ALE. ALE exhibits the same ion-neutral synergy as RIE but the removal amount is not flux dependent due to the separation of the neutral (chemical) and ion fluxes /1,2/. Flux independence gives ALE its most prominent property: inherent uniformity across all length scales – across wafer, loading, ARDE and surface smoothness.

As compared to conventional plasma etching, step separation in ALE also offers a simplified system in which to study the etching mechanisms based on first principles. For example, recently, the process window of ALE was shown to be predictable based on the energy barriers relevant to the substrate-reactant combination, such as the surface binding energies of the chemically modified and bulk material /3/. The separate and independent steps make it particularly suitable to modelling efforts. Here we present the latest results in feature scale modelling of new material systems amenable to the ALE approach as well as experimental results.

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9:20am **PS+NS+SS+TF-ThM5 Thermal Atomic Layer Etching of $VO_2$ Using Sequential Exposures of $SF_4$ and Either $Sn(acac)_2$ or $BCl_3$**, ***Jonas Gertsch***, *V.M. Bright, S.M. George*, University of Colorado Boulder

Thermal atomic layer etching (ALE) is based on sequential self-limiting thermal reactions [1]. Thermal ALE offers a precise and gentle etching procedure and has been demonstrated for many materials including $Al_2O_3$, $HfO_2$, ZnO, $ZrO_2$, $SiO_2$ and AlN [1,2]. This study developed thermal ALE processes for vanadium oxide ($VO_2$). $VO_2$ has a metal-insulator transition at ~68 °C and is useful for thermochromic films and heat-switching devices. The initial $VO_2$ films were deposited using $VO_2$ atomic layer deposition (ALD) with tetrakis(ethylmethylamino) vanadium(IV) (TEMAV) and $H_2O$ as the co-reactants at 150 °C.

The $VO_2$ films were etched using sequential exposures of sulfur tetrafluoride ($SF_4$) and either tin(II) acetylacetonate ($Sn(acac)_2$) or boron trichloride ($BCl_3$) at temperatures ranging from 150-250 °C. *In situ* quartz crystal microbalance studies were used to monitor film growth and etching during the ALD and ALE reactions. The $VO_2$ etching mechanism using $SF_4$ and $Sn(acac)_2$ is observed to occur by fluorination and ligand-exchange reactions [1]. The $SF_4$ exposures yielded mass gains that were consistent with fluorination of $VO_2$ to $VF_4$. The $Sn(acac)_2$ exposures then led to mass losses that were attributed to ligand-exchange reactions that produced volatile acetylacetonate reaction products. $VO_2$ ALE etch rates increased with temperature from 0.04 Å/cycle at 150 °C to 0.27 Å/cycle at 225 °C.

A different reaction mechanism was observed for $VO_2$ ALE using $SF_4$ and $BCl_3$. The $SF_4$ exposures yielded mass losses at all temperatures that were not consistent with simple fluorination of $VO_2$ to $VF_4$. The $BCl_3$ exposures produced mass losses at higher temperatures and slight mass gains at 150 °C. The etching of $VO_2$ by $SF_4$ and $BCl_3$ is believed to occur by a "conversion-etch" mechanism [2]. In the "conversion-etch" mechanism, $BCl_3$ converts the surface of $VO_2$ to a thin $B_2O_3$ layer. $SF_4$ can then remove the $B_2O_3$ layer to produce volatile $BF_3$ and $SO_2$. The $VO_2$ etch rates increased with temperature from 0.06 Å/cycle at 150 °C to 1.9 Å/cycle at 250 °C.

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[2] D. R. Zywotko and S. M. George, "Thermal Atomic Layer Etching of ZnO by a "Conversion-Etch" Mechanism Using Sequential Exposures of Hydrogen Fluoride and Trimethylaluminum", *Chem. Mater.* **29**, 1183-1191 (2017).

9:40am **PS+NS+SS+TF-ThM6 Atomic Layer Etching of $MoS_2$ for Nanodevices**, ***KiSeok Kim***, *K.H. Kim, Y.J. Ji, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Among the layered transition metal dichalcogenides (TMDs) that can form stable two-dimensional (2-D) crystal structures, molybdenum disulfide ($MoS_2$) has been intensively investigated due to its unique properties in various electronic and optoelectronic applications with different band gap energies from 1.29 to 1.9 eV as the number of layers is decreased. To control the $MoS_2$ layers, atomic layer etching (ALE) (which is a cyclic etching consisting of a radical-adsorption step such as Cl adsorption and a reacted-compound desorption step via a low-energy $Ar^+$-ion exposure) can be a highly effective technique to avoid inducing damage and contamination that occur during the cyclic steps. In this study, for the $MoS_2$ ALE, the Cl radical is used as the adsorption species and a low-energy $Ar^+$ ion is used as the desorption species. A $MoS_2$-ALE mechanism (by which the $S_{(top)}$, $Mo_{(mid)}$, and $S_{(bottom)}$ atoms are sequentially removed from the $MoS_2$ crystal structure due to the trapped Cl atoms between the $S_{(top)}$ layer and the $Mo_{(mid)}$ layer) is

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* **Coburn & Winters Student Award Finalist**

reported with the results of an experiment and a simulation. A monolayer $MoS_2$ field effect transistor (FET) fabricated after one-cycle of ALE of a bilayer $MoS_2$ FET exhibited electrical characteristics similar to a pristine monolayer $MoS_2$ FET indicating no electrical damage on the monolayer $MoS_2$ surface after the ALE.

11:00am **PS+NS+SS+TF-ThM10 Ge Atomic Layer Etching for High Performance FinFET**, *W. Mizubayashi,* AIST, Japan, *S. Noda,* Tohoku University, Japan, *Y. Ishikawa, T. Nishi,* AIST, Japan, *A. Kikuchi,* Tohoku University, Japan, *H. Ota,* AIST, Japan, *P.-H. Su, Y. Li,* National Chiao Tung University, Taiwan, *S. Samukawa,* Tohoku University, AIST, Japan, ***Kazuhiko Endo***, AIST, Japan **INVITED**

Ge is a promising material for use as high mobility channel in future CMOS. For 5-nm-node CMOS and smaller, to attain electrostatic controllability of the gate electrode, a multichannel fin structure is utilized. Fin structure formation in Ge FinFETs on GeOI substrates is mainly performed by ICP etchings. However, ICP etching causes plasma induced damages owing to the ultraviolet (UV) light generated from the ICP and charge up by ionized atoms. A concern is that such etching damage reduces the performance and reliability of Ge-channel CMOS. In this work, to break-through these plasma induced damages, we demonstrated defect-free and highly anisotropic Ge etching for Ge FinFET fabricated by Cl neutral beam etching.

There are two advantages in the neutral beam etching process. 1) The wafer is not exposed by the UV light generated from the plasma through the high-aspect-ratio carbon aperture plate. 2) Ions are efficiently neutralized by collision with the carbon aperture plate. Thus, in neutral beam etching, the influences of the UV light and charge-up can be perfectly eliminated and defect-free etching can be realized.

In the ICP etching, the Ge fin is formed but has a trapezoidal shape. On the other hand, the Ge fin in the case of neutral beam etching can be vertically formed as compared with that in the case of the ICP etching. A channel surface with atomic-level smoothness was confirmed in neutral beam etching while some roughness was observed in the ICP etching. In neutral beam etching without UV light irradiation, the Ge surface is not damaged, and a surface dangling bond is formed only on the atomic layer and it undergoes a chemical reaction with the reactive species [1]. Thus, atomic layer etching can be realized by neutral beam etching.

The $|I_d|$–$V_d$ and $|I_d|$–$V_g$ characteristics of the Ge FinFET fabricated by neutral beam etching are markedly improved as compared with those of the FinFETs fabricated by ICP etching, in n- and p-type FinFETs. $g_{m\,max}$ for the Ge FinFET fabricated by neutral beam etching is two times higher for the nFinFET and 10% higher for the pFinFET than those of the FinFETs fabricated by ICP etching, regardless of the fin thickness. In the case of neutral beam etching, since there is no etching damage in the Ge fin, the interface state and surface roughness are drastically lowered. This is the reason for the improved $g_{m\,max}$ for the n- and p-type Ge FinFETs fabricated by neutral beam etching. Thus, the atomic-level flatness and damage-free etching in the Ge fin formation are essential to high performance Ge FinFETs, which can be realized by neutral beam etching.

References

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11:40am **PS+NS+SS+TF-ThM12 Numerical Simulations of Atomic-Layer Etching (ALE) for $SiO_2$ and SiN**, ***Yuki Okada***, Osaka University, Japan, *R. Sugano,* Hitachi, Ltd., Japan, *M. Isobe, T. Ito, H. Li, K. Karahashi, S. Hamaguchi,* Osaka University, Japan

As the sizes of modern semiconductor devices approach near-atomic scales, processing to create such devices in mass production scale also requires atomic-scale precisions. Recent technological advancement for atomic-scale processing includes the development of atomic-layer deposition (ALD) and atomic-layer etching (ALE), in which deposition or etching processes take place layer by layer with each step having self-limiting chemical reactions. In such a process, self-limiting reactions result in not only atomic-scale accuracy of processed structures but also process uniformity over a large area regardless of structure densities. In this study we have examined mechanisms of ALE processes of SiO2 and SiN based on digital or pulsed application of fluorocarbon or hydrofluorocarbon plasmas, using molecular dynamics (MD) simulations. In MD simulations, chemically reactive species and low-energy incident ions are supplied to a SiO2 or SiN surface alternatively. A supply of a certain amount of chemically reactive species to the surface does not spontaneously induce etching reactions. However, when the surface with such reactive species is subject to ion bombardment, energy and momentum supplied to the surface by incident ions activate surface reactions and etching reactions take place. If the ion bombardment energy is sufficiently low, this etching process stops when reactive species are depleted from the surface. In this study, we have examined various combinations of reactive species and ion bombardment. For example, in the case of SiO2, reactive species and ions used in this study are fluorocarbon radicals and low-energy (e.g., 40 eV) Ar+ ions. In the case of SiN, reactive species and ions are hydrogen radicals and low-energy (e.g., 10 eV) Ar+ ions. Also in the case of SiN, we have used simultaneous injection of hydrogen radicals with low energy CF3+ ion bombardment as a radical supply process and low-energy (e.g., 50 eV) Ar+ ion injections as a process to remove excess fluorocarbon deposited on the surface. In the last case, etching self limit occurs because of accumulation of a fluorocarbon layer, rather than the removal of it. It has been found that, in most cases, the complete removal of reactive species from the surface is not easy and the control of remaining reactive species on the surface after each digital process step is the key for the success of ALE process development.

12:00pm **PS+NS+SS+TF-ThM13 Organometallic Etching Chemistry for Thermal Atomic Level Etching of Lanthanum Oxide**, ***Yoshihide Yamaguchi***, *K. Shinoda,* Hitachi, Japan, *Y. Kouzuma, S. Sakai, M. Izawa,* Hitachi High-Technologies Corp., Japan

The demand for thermal atomic level etching (ALEt) of a wide variety of materials including silicon-based materials, metals, and high-k materials is increasing as semiconductor device geometries continue to shrink. To meet the increased demand, remarkable progress into ALEt research has been made in the last few years. One example is the pioneering research on the thermal ALEt of hafnium oxide emerged [1], where hafnium oxide sequentially reacted with HF and a stannous organometallic compound (Sn(acac)2). Thermal ALEt of SiN is another example [2][3], where sequential reactions of a plasma-assisted self-limiting surface modification and a thermal desorption of the self-limiting layer was employed.

In this work, we present our challenge for the thermal ALEt of lanthanum oxide by using surface modification followed by thermal desorption. A key technology of this ALEt is the novel organometallic chemistry for the one-step surface modification of lanthanum oxide. A lanthanum oxide sample exposed to gas of fluorine-containing ketone together with a stabilizer led to the formation of volatile organic species on the sample surface, while a SiO2 sample remained unchanged under the same process condition. The gas-exposed lanthanum oxide sample was then annealed at elevated temperatures under vacuum to remove the volatile species from the surface. After these consecutive processes, the volatile organic species from the lanthanum oxide sample were collected and identified by nuclear magnetic resonance (NMR) spectroscopy and infrared (IR) spectroscopy. These results indicated that the volatile species was an organo-lanthanum complex bearing the fluorine-containing ketone moiety as the ligand. On the basis of these results, a novel selective dry-chemical removal of lanthanum oxide was successfully demonstrated.

Several results on selective dry-chemical removal of lanthanum oxide with respect to TiN, metal oxide, and some other material will also be disclosed.

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## Plasma Science and Technology Division
## Room: 22 - Session PS-ThM

### Plasma Sources

**Moderators:** Rebecca Anthony, Michigan State University, David Ruzic, University of Illinois at Urbana-Champaign

8:00am **PS-ThM1 New Plasma Source Generating High Radical Flux With Low Ion and Photon Flux**, *Y. Pilloux,* ***David Lishan***, *M. Segers,* Plasma-Therm LLC

Substrate cleaning of organics utilizes a range of technologies that includes wet processing, barrel ashers, and microwave driven downstream plasmas. In this work, we introduce a unique inductively coupled downstream source configuration to generate high density radical concentrations (>1.1E+17 $cm^{-3}$) but without high ion and photon fluxes typically found in conventional inductively coupled plasmas. Although the plasma discharge tubes are isolated from the treatment chamber, they deliver a large concentration of free radicals. The low ion and photon exposure significantly reduces the opportunity for damage to sensitive layers. This inductive plasma arrangement prevents local heating and charging on the wafer, and behaves similarly as a microwave downstream plasma. However, a higher oxygen radical flux promotes more efficient organic layer cleaning and/or removal of photoresists even when low thermal budgets are a constraint.

This work will first describe the High Density Radical Flux (HDRF) source and characterize its behavior in generating high radicals flow and low ions in local downstream, on the wafer surface. Second, several applications using the HDRF technology will be discussed. These applications will include cleaning of 30:1 aspect ratio (AR) silicon vias, removal of sacrificial layers in MEMS structures, low temperature photoresist removal, and surface smoothing of Bosch generated sidewalls using micro-isotropic etching. With a low local electrical potential, due to the limited ions present in the process chamber, the HDRF is particular efficient with 3D structures on the wafer (e.g. MEMS and other high AR features) where preventing ion shielding effects is important.

8:20am **PS-ThM2 Towards Plug-and-Play Tailored Voltage Waveform Plasma Sources: Progress in Matching and Calibration**, ***Erik V. Johnson***, LPICM, Ecole Polytechnique, France, *K. Yamaki*, LPP-CNRS, *J.-P. Booth*, LPP-CNRS, Ecole Polytechnique, France

The use of non-sinusoidal Tailored Voltage Waveforms (TVWs) to excite a plasma process has proven to be a rich field. Performing deposition or etching using such TVWs been shown to provide (1) a greater degree of control over outcomes, (2) more understanding of those processes, and even (3) processes unachievable by any other means, such as electrode-selective deposition.

The dream design for a Tailored Voltage Waveform plasma source is one that can ensure that an exact version of a given waveform appears on the RF electrode, but without increasing the complexity and cost of the source far beyond that of a single frequency RF source (including matchbox). These requirements are challenging due to the multi-harmonic nature of TVW's; the matching network must simultaneously provide efficient impedance matching at multiple frequencies, and as the phase between harmonics matters, for certain systems the waveform appearing at the RF feedthrough will not be a scaled version of the one on the electrode.

We address these two challenges directly. For the multi-frequency impedance matching challenge, we present progress on the design and fabrication of a high-power multi-frequency matchbox. This system allows the semi-independent tuning of the matching condition at each harmonic. For the second challenge involving uncertainty in the waveform appearing at the electrode, we present results using the plasma properties themselves to eliminate potential sources of error in the waveform. This technique avoids the need for probes located within the vacuum chamber, optical access to the plasma, or limiting the waveforms to lower frequencies.

8:40am **PS-ThM3 Selective Radical Production in Remote Plasma Sources**, ***Shuo Huang***, University of Michigan, *V. Volynets, S. Lee, S. Nam, S. Lu*, Samsung Electronics Co. Ltd., Republic of Korea, *M.J. Kushner*, University of Michigan

Remote plasma sources (RPS) are being used to achieve isotropic etching with high selectivity by avoiding charging, energetic ion bombardment and UV/VUV radiation using long distance and discriminating barriers between the RPS and the substrate. By using multiple plasma sources or multiple gas inlets at different locations, the reaction pathway can be optimized for producing desirable process radicals. $NF_3$ and HBr are frequently used sources of F and Br atoms, the main etchants of silicon-containing materials, by electron impact dissociative attachment and excitation. $NF_x$ ($x = 1 – 3$) and HBr can exothermically react with other neutral species to produce F, Br and OH radicals, which also enables customizing the reaction pathway by flowing gases downstream of the RPS.

In this paper, we report on results from a computational investigation of an inductively coupled RPS having multiple gas inlets with the goal of determining strategies for selectively producing reactive fluxes. The investigation was performed using the plug flow mode of 0-dimensional model, Global_Kin and in 2-dimensions using the Hybrid Plasma Equipment Model (HPEM). With $NF_3/N_2/O_2$ mixtures flowed through the RPS from an upstream inlet, the dominant radicals flowing downstream are F and O formed through dissociative excitation and attachment of $NF_3$ and $O_2$. NO molecules were formed through endothermic reactions among $N_2$, N, $O_2$ and O species. With HBr injected downstream of the plasma source, mixing with the plasma produced radicals enable another level of selectivity. Due to lack of electrons and low gas temperature (~ 350 K) downstream, HBr reacts with F and O through exothermic reactions (HBr + F > HF + Br, HBr + O > OH + Br and HBr + OH > $H_2O$ + Br) and the dominant downstream radicals transition from F and O to Br and HF. Vibrationally excited HF(v), a highly polar molecule, may be formed through reactions having a larger exothermicity than the vibrational quanta, and so may produce a significant flux of activation energy to the wafer

Work was supported by Samsung Electronics, DOE Office of Fusion Energy Science and the National Science Foundation.

9:00am **PS-ThM4 On Electron Heating in Magnetron Sputtering Discharges**, ***Jon Tomas Gudmundsson***, University of Iceland, *D. Lundin*, Université Paris-Sud, France, *M.A. Raadu*, KTH-Royal Institute of Technology, Sweden, *T.M. Minea*, Université Paris-Sud, France, *N. Brenning*, KTH-Royal Institute of Technology, Sweden

The magnetron sputtering discharge has been applied successfully in various industrial functions for over four decades. Sustaining a plasma in a magnetron sputtering discharge requires energy transfer to the plasma electrons. In the past, the magnetron sputtering discharge has been assumed to be maintained by cathode sheath acceleration of secondary electrons emitted from the target, upon ion impact. These highly energetic electrons then either ionize the atoms of the working gas directly or transfer energy to the local lower energy electron population that subsequently ionizes the working gas atoms. This is the essence of the well-known Thornton equation, which in its original form [1] is formulated to give the minimum required voltage to sustain the discharge. However, recently we have demonstrated that Ohmic heating of electrons outside the cathode sheath is typically of the same order as heating due to acceleration across the sheath in dc magnetron sputtering (dcMS) discharges [2]. The secondary electron emission yield $\gamma_{\mathrm{see}}$ is identified as the key parameter determining the relative importance of the two processes. In the case of dcMS Ohmic heating is found to be more important than sheath acceleration for secondary electron emission yields below around 0.1. For the high power impulse magnetron sputtering (HiPIMS) discharge we find that direct Ohmic heating of the plasma electrons is found to dominate over sheath acceleration by typically an order of magnitude, or in the range of 87 – 99 % of the total electron heating. A potential drop of roughly 80 - 150 V, or 15 - 25% of the discharge voltage, always falls across the plasma outside the cathode sheath [3]. We also discuss the influence of the magnetic field strength on the discharge properties.

[1] J A Thornton, J. Vac. Sci. Technol. 15 (1978) 171

[2] N. Brenning et al., Plasma Sources Sci. Technol. 25 (2016) 065024

[3] C Huo et al., Plasma Sources Sci. Technol. 22 (2013) 045005

9:20am **PS-ThM5 High-Density Plasma Generation in Low-Pressure Metamaterial Space**, ***Osamu Sakai***, The University of Shiga Prefecture, Japan **INVITED**

Generation of high-density plasmas have been one of the main topics in science and technology of low-temperature plasma since high throughputs in material processing such as dry etching and thin-film deposition are achieved by high electron density which enhances chemical and physical processes in weakly-ionized plasma. When we use microwaves in plasma generation, there have been several methods proposed so far for high-density plasma, like electron-cyclotron-resonance plasma and surface-wave plasma.

Here we propose another scheme in which a magnetic metamaterial makes magnetic permeability in discharge space negative. Microwave propagation in simple discharge space with no objects and no external magnetic field is limited by cutoff density where electric permittivity or dielectric constant is down to zero. When magnetic metamaterial who has negative permeability is installed in the space, microwave propagation is possible beyond the cutoff density, with negative refractive index state with negative permittivity that indicates high electron density. Experimental observation confirmed existence of this scheme, and electron density was much higher than the cutoff density (approximately $7x10^{10}$ $cm^{-3}$ when microwave frequency is 2.45 GHz) [1]. The value of electron density has no limitation with smooth microwave propagation with large negative values of refractive index.

In addition to these advantages on generation of high-electron-density plasma, recent experimental studies have revealed that this scheme of plasma generation has roles of high energy storage and an efficient energy converter. From the estimations based on monitored electron density and temperature, the existing energy density in the plasma generation space with the metamaterial is by 3 orders of magnitude larger than that in microwave propagation in the free space. Such stored energy is efficiently converted into the second harmonic wave via nonlinear and asymmetry effects between plasma and metamaterial [2], as well as into chemical energy via enhanced dissociation of gas molecules. These facts indicate that this plasma source will contribute to novel functions that can be hardly established using other plasma generation schemes as well as the general function as a high-density plasma source for material processing.

[1] O. Sakai, Y. Nakamura, A. Iwai and S. Iio, Plasma Sources Sci. Technol. 25 (2016) 055019.

[2] A. Iwai, Y. Nakamura and O. Sakai, Phys. Rev. E 92 (2015) 033105.

11:00am **PS-ThM10 Optical Emission Spectroscopy of a Spark-coupled Laser Aluminum Plasma for Multicharged Ion Generation**, ***Md Mahmudur Rahman***, *O. Balki, M. Shaim, H.E. Ali*, Old Dominion University

A spark-coupled laser plasma is used to generate multicharged ions. A Q-switched Nd:YAG laser ($\lambda$ = 1064 nm, , $\tau$ = 8 ns, pulse energy ≤ 100 mJ, repetition rate 1 Hz) ablates an aluminum target creating a laser ion source, while the spark discharge further enhances ion generation. A high-voltage pulse-forming network produces up to 12 kV, ~1 μs pulse across the spark electrodes. Line emission from neutrals and ions are probed by optical emission spectroscopy. These spectral lines are used to obtain time-integrated, spatially-resolved electron temperature ($T_e$) from the Boltzmann plot and electron density ($n_e$) from Stark broadening. The pulse forming network is triggered with a thyratron through a delay in order to optimize the timing between the laser pulse and the spark discharge for best spark energy coupling to the laser plasma. A delay of 100 ns is found to produce the best coupling of the spark energy to the laser plasma. For a spark energy of 1.5 J, the intensity of the Al IV 372.6 nm and Al III 361.2 nm lines increases by a factor of ~10 and ~ 6, respectively compared to that from the laser plasma alone. The effective ion temperature ($T_{ieff}$) associated with translational motion along the plume axis is calculated from the ion time-of-flight (TOF) signal and compared with $T_e$. The results show that $T_{ieff}$ is much larger than $T_e$, although the plasma is considered to be in local thermodynamic equilibrium. This result is explained in view of the different regions of the plasma probed by ion TOF and optical spectroscopy.

11:40am **PS-ThM12 Effect of Secondary Electrons on the Ionization Dynamics and Control of Ion Properties in Electronegative Capacitive Discharges**, ***Aranka Derzsi***, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Hungary **INVITED**

The realization of the separate control of the ion flux and ion energy distribution at the substrate in capacitively coupled radio frequency (RF) discharges is an important issue for various applications of plasma processing, ranging from plasma based etching and deposition procedures in the semiconductor industry to plasma assisted surface treatment of medical interest. In order to attain such independent control of the ion properties, the application of non-sinusoidal voltage waveforms (pulse-like, or saw-tooth-type, for instance), known as „tailored" or „customized" RF voltage waveforms for the excitation of capacitive RF discharges, has recently been introduced. Such waveforms differ from the conventionally applied sinusoidal voltages by exhibiting different absolute values of their positive and negative extrema. This control method is based on the electrically asymmetric plasma response, known as the Electrical Asymmtery Effect, observed when non-sinusoidal exciting voltage waveforms are applied, leading to the generation of a dc self-bias voltage in a geometrically symmetric discharge cell. The applications of tailored voltage waveforms, generated by using multiple harmonics of a base frequency (multi-frequency excitation), offer new possibilities for controlling plasma properties. Most of the systematic studies on capacitive RF plasmas excited by tailored voltage waveforms have been conducted so far in electropositive capacitive RF discharges. However, the applications usually require complex mixtures of reactive gases. For instance, oxygen is widely used in etching and thin film deposition techniques, $CF_4$ is also frequently applied to etch silicon and silicon-dioxide in microelectronics.

Secondary electrons generated at the electrodes are known to influence the ionization dynamics and induce transitions of the discharge operation mode from the α-mode to the γ-mode in electropositive discharges at high driving voltage amplitudes and/or pressures. In electropositive discharges these γ-electrons influence the quality of the separate control of ion properties. Here, we report our systematic simulation studies of the effect of secondary electrons on the electron power absorption and ionization dynamics and on the quality of the separate control of ion properties at the electrodes in low-pressure capacitively coupled RF discharges operated in reactive, electronegative gases excited by tailored voltage waveforms.

## 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.

## Advanced Surface Engineering Division
## Room: 11 - Session SE+PS+SS-ThM

## Plasma-assisted Surface Modification and Deposition Processes

**Moderators:** Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Suneel Kodambaka, University of California at Los Angeles

8:00am **SE+PS+SS-ThM1 Key Features of Reactive High Power Impulse Magnetron Sputtering**, ***Daniel Lundin***, CNRS/Paris-Sud University, France **INVITED**

For many thin film applications, such as optical coatings, energy-related coatings, hard coatings, etc., the coated layers are not single metal thin films, but rather compound coatings obtained from at least one metal (e.g. Al, Ti) or a non-metal (e.g. C, B) and a reactive gas (e.g. $O_2$, $N_2$). This talk will address the challenges and possibilities of depositing compound coatings using a promising thin film deposition technology called high power impulse magnetron sputtering (HiPIMS), and how this method differs from conventional processes. Both nitride and oxide systems will be covered during different modes of operation including pure argon, metallic, transition, and compound modes. Key features in reactive HiPIMS, such as eliminated/reduced hysteresis, stable high-rate deposition in the transition mode, and self-sputter recycling versus working gas recycling, will be addressed by using results from recent plasma process modelling in combination with experimental plasma characterization. Ionization of the material flux will be discussed in detail, since it enables effective surface modification via ion etching and self-ion assistance during film growth, as well as being a key feature in HiPIMS. This includes exploring the temporal evolution of the discharge plasma parameters, such as electron density and temperature, the neutral and ion composition, the ionization fraction of the sputtered vapor as well as of the reactive gas mixture, and the composition of the discharge current. The focus will be on identifying dominating physical and chemical reactions in the plasma and on the surfaces of the reactor affecting the plasma chemistry.

8:40am **SE+PS+SS-ThM3 Depositions of $Al_2O_3$ Coatings by HiPIMS via Closed-loop Control using a Plasma Emission Monitoring Sensor**, ***Jianliang Lin***, *R. Wei, K. Coulter,* Southwest Research Institute, *F. Papa*, Gencoa Ltd.

Reactive sputtering of insulating oxide coatings, e.g. alumina ($Al_2O_3$),by high power impulse magnetron sputtering (HiPIMS) is of great interest, as the increased target ionization in HiPIMS can be used for improving the structure and properties of the coatings. Typically there are two challenges for the process including arc suppression and overcoming the decreased deposition rate due to target poisoning. In this paper, $Al_2O_3$ coatings were reactively sputtered by HiPIMS with deep oscillatory pulses using closed-loop control of oxygen partial pressure to achieve high deposition rates. Stable and Arc-free deposition processes were obtained with a peak target current density up to 1.2 $Acm^{-2}$ by optimizing key pulsing parameters of deep oscillating pulses. The closed-loop control was achieved by controlling oxygen partial pressure from a remote plasma emission monitoring (PEM) sensor which ionizes sample plasma away from the deposition zone. The deposition rate, microstructure and properties of the $Al_2O_3$ coatings deposited at different oxygen partial pressures and HiPIMS peak target current densities were investigated and compared to those obtained by traditional pulsed dc.

9:00am **SE+PS+SS-ThM4 The Influence of Spokes on Spatial and Energy Distributions of Ions in Magnetron Sputtering Discharges**, ***Matjaz Panjan***, Jozef Stefan Institute, Slovenia, *K. Tanaka, R. Franz, A. Anders*, Lawrence Berkeley National Laboratory

The formation of dense plasma structures, called ionization zones or spokes, is now a well documented phenomenon in magnetron discharges [1,2]. Experiments and models suggest that these structures strongly influence the transport and the energy of electrons and ions [3,4]. Previously, we measured ion energy distribution functions in the plane of the magnetron by moving its target surface sideways with respect to the orifice of a combined mass spectrometer and energy analyzer (EQP300, Hiden Ltd.) [5]. The measurements showed asymmetric flux of ions in the plane of the target, which was attributed to the moving spokes. Here we report on the measurements of ion energy distribution functions for two different magnetron-EQP arrangements. In the first experimental arrangement, the orifice of EQP300 was directed in the plane of the magnetron and the magnetron was moved in the axial direction. In the second arrangement, the magnetron was rotated around its center for different polar angles while the distance between the target and the orifice was fixed. Measurements were performed in direct current magnetron sputtering (DCMS) using a 3" magnetron and niobium target. Ion energy distribution functions were measured for single and double charged argon and niobium ions. The first experiment showed that the largest flux of high-energy ions (i.e. ions above 10 eV) exists around 30 mm above the target. Overall, higher fluxes were observed in the **E**×**B** direction than in the -**E**×**B** direction. Polar measurements showed larger ion fluxes and higher ion energies near the target plane as compared to considerably lower fluxes and energies perpendicular to the target. The results of the measurements are discussed with respect to the plasma potential structure and associated electric field distribution of a rotating spoke, which we recently measured in DCMS discharge [6].

[1] A. Anders *et al.*, *J. Appl. Phys.*, **111** (2012) 053304

[2] M. Panjan *et al.*, *Plasma Sources Sci. Technol.*, **24** (2015) 065010

[3] R. Franz *et al.*, *Plasma Sources Sci. Technol.*, **25** (2016) 015022

[4] A. Anders, *Appl. Phys. Lett.*, **105** (2014) 244104

[5] M. Panjan *et al.*, *Plasma Sources Sci. Technol.*, **23** (2014) 025007

[6] M. Panjan and A. Anders, *J. Appl. Phys.***121** 063302 (2017)

9:20am **SE+PS+SS-ThM5 Silicon Nitride Deposition for Organic Electronics by VHF (162MHz)- PECVD**, *G.Y. Yeom*, ***KiHyun Kim***, *K.S. Kim, Y.J. Ji, J.S. Oh*, Sungkyunkwan University, Republic of Korea

Deposition of permeation barrier film for organic-based electronics is one of the most important issues in organic electronic device fabrication process because the permeation of moisture and oxygen into organic materials causes significant degradation of the device performance and stability. In this study, as an effective thin film barrier material for organic electronics, we investigated low-temperature (~ 80 °C) silicon nitride deposited by very high frequency (VHF, 162MHz) PECVD using multi-tile push-pull electrodes with a gas mixture of $NH_3/SiH_4$. The composition of the silicon nitride film deposited by VHF PECVD was similar to the ideal stoichiometry of silicon nitride (Si : N = 1 : 1.33) and the deposited film exhibited high optical transparency over 90% in the visible region. The deposited silicon nitride also exhibited a high step coverage of 1:1.29. When water vapor transmission rate (WVTR) was measured with single (400 nm thick) $SiN_x$ layer deposited on PET, excellent WVTR of $4.39 \times 10^{-4}$ $g/m^2\cdot day$ could be obtained. I-V characteristics of organic light emitting diode (OLED) devices were measured before and after the film deposition on the devices, and no noticeable changes of I-V characteristics after the deposition of silicon nitride film on the OLED devices were observed indicating no noticeable electrical damage by the deposition of silicon nitride using VHF PECVD which is ascribed by low electron temperature characteristics of the plasma and the lack of current flow to the substrate for the VHF-PECVD method utilizing multi-tile push-pull-type electrodes.

Keywords : encapsulation, silicon nitride, organic light emitting diode (OLED), very high frequency (VHF), water vapor transmission rate (WVTR), step coverage

9:40am **SE+PS+SS-ThM6 Printed Circuit Board Assembly- an Ensemble of Different Surface Energy Components and their Surface Modification**, ***Shailendra Vikram Singh***, *S. Woollard, G. Aresta, A.S. Brooks, G. Hennighan*, R&D Semblant Limited

Plasma-produced thin film liquid ingress barrier coatings for electronic devices have several advantages over conventional parylene-based coatings. However, issues connected with plasma processing conditions, electronic device casing designs, and manufacturing technicalities and throughput, independently or in combination, may limit appropriate implementation of such coatings. Hence, it is critical to apply such coatings directly on the printed circuit board assembly (PCBA) of a device to achieve excellent protection against liquid ingress damages. Moreover, an additional coating on the device case can provide extra features and advantage. A PCBA is a complicated substrate in terms of conformality and adhesion requirements. It comprises an ensemble of different surfaces of different shapes and sizes and various materials: metals, polymers, polyester (fiber and resins), graphite, solder residue, etc. The surface energies of these components on boards vary from ~10 mN/m to up-to ~70 mN/m. In this study, we have addressed the surface treatment and etch cleaning requirements for better adhesion of a reworkable conformal plasma coating. The main challenge resides in altering the surface energy consistently across all the surfaces present on a PCBA. Furthermore, in a manufacturing situation the chance of surface contamination due to handling is very high. Especially, in our case, where, the manufacturing speed is >700 standard phone PCBAs/hr/coater batch. Surface chemistry, type and amount of such randomly introduced contaminations cannot be easily predicted. In this regard, we have also studied several hypothetical contamination situations investigating the relationship between etch-clean and surface energy change.

11:00am **SE+PS+SS-ThM10 Plasma Surface Engineering of Biomaterials**, ***Paul K. Chu***, City University of Hong Kong, Hong Kong **INVITED**

The chemical and biological interactions between biomaterials and biological tissues depend on the surface properties of the biomaterials and associated biological responses. However, many types of biomaterials that possess favorable bulk properties such as hardness, strength, robustness may not perform the pre-designed biological functions and so surface modification is frequently performed to enhance the biological and chemical properties. Plasma-based technology offers the unique capability that selected surface properties can be modified to address specific biological requirements while the desirable bulk properties of the materials such as those mentioned above are preserved. In particular, plasma immersion ion implantation and deposition (PIII&D) is one of the widely used plasma-based surface techniques suitable for biomaterials and biomedical devices. Being a non-line-of-sight technique, it is especially suitable for biomedical devices with a complex shape like dental and orthopedic implants, scoliosis correction rods, cardiovascular stents, and artificial heart valves. In this invited presentation, recent research performed in the Plasma Laboratory of City University of Hong Kong related to plasma treatment of biomaterials and biomedical devices will be described. Examples include biocompatibility of nanostructured surfaces and coatings, biocompatibility of biodegradable materials, bacterial resistance, as well as osseointegration and osteogenesis.

12:00pm **SE+PS+SS-ThM13 Tuning the Properties of Plasma Polymer Varying the Substrate Temperature: a Step Toward the Fabrication of Micro/nano Pattern**, ***Damien Thiry***, University of Mons, Belgium, *N. Vinx, F.J. Aparicio*, University of Mons, *T. Godfroid, S. Deprez*, Materia Nova, *R. Snyders*, University of Mons, Belgium

Plasma polymerization is a well-known technique developed during the last decades for the development of solid organic functionalized thin films (100nm - 1µm) from a large range of organic precursors. The retention of the precursor functionalities and the synthesis of soft material has rapidly become a challenge in the field. The usual strategy consists in limiting the fragmentation of the precursor in the plasma by reducing the load of energy in the discharge. In this work, an almost unexplored approach based on varying the substrate temperature for a given set of plasma parameters is studied in order to extend the control that plasma polymerization provides over the cross-linking degree and the chemical composition of the formed layers. As a case study, propanethiol plasma polymer films (Pr-PPF) finding application as support for gold nanoparticles and biomolecules immobilization are investigated.

The deposition rate of Pr-PPF was found to follow an Arrhenius law with the substrate temperature ($T_s$) varying from -10 °C to 45°C. This behavior is explained through the influence of $T_s$ on the residence time of the film-forming species at the growing film interface. With regard to the chemical composition of the layers, the atomic sulfur content is nearly constant (i.e. ~ 45 at. %) in the range $-10\ °C < T_s < 23\ °C$ and strongly decreases (i.e. ~ 30 at. %) for $T_s > 23\ °C$. Based on these data, it can be proposed that a critical $T_S$ has to be reached for favouring the desorption of sulfur-based species before their incorporation within nascent plasma polymer. On the other hand, "rough" indentations measurements combined with optical microscopy imaging reveal that for $T_s < 10°C$, a deformation of the Pr-PPF takes place when applying a force (i.e. 1 mg) on the top of the polymer with the tip of the profilometer. Furthermore, a fast recovery of the plasma polymer layer occurs over a time scale of about 3 min. As an important result, these data disclose the possibility to produce soft and visco-elastic plasma polymer layer. Finally, inspired by the wrinkling phenomenon occurring in a bilayer system exhibiting a high contrast in terms of mechanical properties, a thin aluminium coating is deposited by magnetron sputtering on the top of a low cross-linked Pr-PPF synthesized at $T_s = 10°C$. The mismatch between the mechanical properties between both layers results in the formation of a wrinkled surface. By tuning the thickness of the aluminium and the Pr-PPF coatings, the height (i.e. from 0.4 to 5.2 µm) and the width (i.e. from 0.6 µm to 6.5 µm) of the nano/micro objects can be easily tailored offering a great flexibility in terms of nano/micro engineering.

## 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.

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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$_2$O$_3$(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 ($\alpha$-Fe$_2$O$_3$) 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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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.

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## Thin Films Division
## Room: 20 - Session TF+SE-ThM

## Control, Characterization, and Modeling of Thin Films I
**Moderators:** Hilal Cansizoglu, University of California, Davis, Tansel Karabacak, University of Arkansas at Little Rock

8:00am **TF+SE-ThM1 *In Situ* Synchrotron Characterization Techniques Enabled Nanostructured Materials using ALD**, ***Yu Lei***, University of Alabama in Huntsville

To achieve the goal of rational design of next generation of advanced materials, we have been working on developing atomic layer deposition (ALD) as a promising method to tailor size and composition of nanostructured materials for a wide range of applications. Benefiting from self-limiting surface reactions, ALD enables conformal coatings of materials on three-dimensional substrates. The atomic level control of depositions makes it attractive to precisely synthesize the size and composition of nanomaterials. The size and composition of nanomaterials play important roles in achieving high performance in many applications. In this talk, we will discuss nanomaterials synthesized using Pd ALD and their applications in catalysis and energy storage. We will also illustrate that *in situ* characterization techniques such as synchrotron X-ray based X-ray absorption spectroscopy (XAS), X-ray pair distribution function (PDF), and FT-IR significantly advance our understandings of ALD in terms of surface chemistry and surface dynamics.

8:20am **TF+SE-ThM2 Probing the Atomic Scale Structure of Polar Oxide Interfaces**, ***Sanaaz Koohfar***, *D.P. Kumah*, North Carolina State University

Complex oxide heterostructures possess a wide range of functional electronic and magnetic properties including metal-insulator transitions, superconductivity, ferroelectricity and colossal magnetoresistance effects. At epitaxial interfaces formed between atomically thin complex oxide films, electronic, chemical and structural interactions can be used to effectively tune the physical properties of these materials. Using a combination of atomic-scale controlled thin film synthesis and high resolution synchrotron diffraction based imaging, we show that structural distortions at the interfaces between polar $La_{1-x}Sr_xMnO_3$ films and non-polar substrates can be effectively tuned by chemical modifications at these interfaces to control ferromagnetism in [001]-oriented $La_{1-x}Sr_xMnO_3$ films with thickness less than 1 nm. We show that atomic-scale chemical control at polar/non polar oxide interfaces provides a powerful route to engineer novel electronic and magnetic phenomena at complex oxide interfaces.

8:40am **TF+SE-ThM3 CVD Chemistry of Trimethylboron - Gas Phase Reactions and Surface Poisoning Effects**, ***Henrik Pedersen***, *L. Souqui, M. Imam*, Linköping University, Sweden, *R. Tonner*, Philipps Universität Marburg, *H. Högberg*, Linköping University, Sweden

Organoborons with short alkyl groups; trimethylboron (TMB), $B(CH_3)_3$, triethylboron (TEB), $B(C_2H_5)_3$, and tributylboron (TBB), $B(C_4H_9)_3$, were suggested as alternative, highly reactive, less-poisonous, non-explosive B-precursors in the mid 1990's[1].TEB was found to exhibit the best properties for CVD of boron-carbon films, making it a popular CVD precursor[2]. TMB and TBB were deemed not suitable as CVD precursors as no boron was found in the films deposited from these molecules. Consequently, these molecules are less investigated in CVD.

We study the gas phase chemistry of TMB in a thermal CVD process, using a combination of B-C film deposition experiments at several temperatures in both hydrogen and argon atmosphere and quantum chemical calculations for a wide range of possible gas phase reactions. We suggest that without assistance from the carrier gas, i.e. in argon ambient, TMB most likely decomposes by α-H elimination of $CH_4$ to form $H_2CBCH_3$. Methane is not highly reactive in CVD at deposition temperatures below 1000 °C, meaning that the $H_2CBCH_3$ species is the major film forming species. This correlates well with the B/C ratio of about 0.5 observed for films deposited in Ar at 700-900 °C. At higher temperatures, the B/C ratio of films increases as attributed to further decomposition to $H_2BCH_3$.

With assistance from the hydrogen carrier gas, TMB can also decompose to $HB(CH_3)_2$ that can further decompose to $H_2BCH_3$ and finally to $BH_3$, all with negative Gibbs free energies, albeit with some high energy barriers. This in combination with the unimolecular α-H elimination with a somewhat lower energy barrier, can explain the higher B/C ratios of films deposited in $H_2$.

Furthermore, we note that the onset of film deposition from TMB is 700 °C and at then at a very low deposition rate. Interestingly the film thickness does not increase with longer deposition time at 700 °C, indicating a surface poisoning effect. As this is seen both in Ar and $H_2$, we speculate that this is caused by $CH_4$ or $H_2CBCH_3$, which is currently the subject of our further investigations.

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[2] M. Imam et al. Gas phase chemical vapor deposition chemistry of triethylboron probed by boron–carbon thin film deposition and quantum chemical calculations. *J. Mater. Chem. C* **2015**, *3*, 10898.

### 9:20am **TF+SE-ThM5** ***In Situ* Synchrotron-based Characterization of Noble Metal ALD Processes**

*J. Dendooven*, ***Eduardo Solano***, *R.K. Ramachandran, M.M. Minjauw*, Ghent University, Belgium, *A. Coati*, Synchrotron SOLEIL, France, *D. Hermida-Merino*, ESRF, France, *C. Detavernier*, Ghent University, Belgium **INVITED**

Supported noble metal nanoparticles (NPs) are widely used in heterogeneous catalysis because of their high resistance against chemical poisoning. Atomic Layer Deposition (ALD) can be used to synthesize noble metal NPs on different high surface area supports, and offers sub-monolayer control over the metal loading (atoms per $cm^2$ of support) [1]. However, an improved understanding of how the deposition parameters influence the formation and growth of noble metal NPs is required to fully exploit the tuning potential of ALD.

We developed a synchrotron-compatible high-vacuum setup that enables in-situ monitoring during ALD [2]. Using this setup and focusing on ALD of Pt with the $MeCpPtMe_3$ precursor at 300 °C [3], we present an in-situ investigation of Pt NP growth on planar $SiO_2$ substrates by means of X-ray fluorescence (XRF) and grazing incidence small-angle X-ray scattering (GISAXS). The surface density of Pt atoms was determined by XRF. Analysis of the GISAXS patterns [4] yielded dynamic information on average real space parameters such as Pt cluster shape, size and spacing. The results indicate a diffusion-mediated particle growth regime for the standard $O_2$-based Pt ALD process, marked by a decreasing average areal density and formation of laterally elongated Pt clusters. Growth of the Pt NPs is thus not only governed by the adsorption of Pt precursor molecules from the gas-phase and subsequent combustion of the ligands, but is largely determined by adsorption of migrating Pt species on the surface and diffusion-driven particle coalescence [5].

Next, we have studied the influence of the reactant type ($O_2$ gas, $O_2$ plasma, $N_2$ plasma, $NH_3$ plasma [6]) on the Pt NP growth. Surprisingly, a clear difference in island growth behavior was found for the oxygen- vs. nitrogen-based processes. The latter processes were marked by a constant average particle distance during the growth process. Particle dimension analysis furthermore revealed vertically elongated NPs for the $N_2$ and $NH_3$ plasma-based Pt ALD processes. Therefore, it is concluded that atom and cluster surface diffusion phenomena are suppressed during the nitrogen-based processes. Finally, this insight provided the ground for the development of a tuning strategy that is based on combining the $O_2$-based and $N_2$ plasma-based ALD processes and offers independent control over NP size and coverage.

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### 11:00am **TF+SE-ThM10** ***In-situ* FTIR Study of the Atomic Layer Deposition of Scandium Oxide Films using Bis(methylcyclopentadienyl)3,5-dimethylpyrazolatoscandium with Ozone and with Water**

***Rezwanur Rahman***, *J.P. Klesko, A. Dangerfield*, University of Texas at Dallas, *J.-S. Lehn, C.L. Dezelah, R. Kanjolia*, EMD Performance Materials, *Y.J. Chabal*, University of Texas at Dallas

Scandium oxide ($Sc_2O_3$) thin films have been thoroughly studied for their use in microelectronic devices.$^{1–2}$ However, processes for the atomic layer deposition (ALD) of $Sc_2O_3$ films are scarce, and have mostly involved $Sc(thd)_3$,$^1$ $ScCp_3$,$^1$ $Sc(MeCp)_3$,$^2$ and $Sc(amd)_3$$^3$ precursors. To date, the only mechanistic investigation has focused on the $Sc(MeCp)_3/H_2O$ process using *in-situ* time-resolved quadrupole mass spectrometry to probe the $Sc_2O_3$ ALD chemistry.$^2$

Herein, we have explored the $Sc_2O_3$ ALD using bis(methylcyclopentadienyl)3,5-dimethyl pyrazolatoscandium ($Sc(MeCp)_2(Me_2pz)$) with ozone and with $D_2O$. This precursor reacts with hydroxyl-terminated silicon, Si(111)– $SiO_2$–OH, at 150 °C and appears to remain thermally stable to 450 °C. Between 225 and 275 °C, there is a clear ligand exchange with ozone observed in the differential IR absorption spectra involving the formation of intermediate formate and carbonate species (1400–1600 $cm^{-1}$) after each ozone pulse. A short incubation period ($\leq 5$ ALD cycles) is observed at 225 °C prior to the onset of steady-state ligand exchange. The signature for the formation of Si–O–Sc bonds (1240 $cm^{-1}$) is clearly present after cycles 1–2 for the ozone process at 275 °C. The $Sc_2O_3$ growth is quantified by X-ray photoelectron spectroscopy (XPS) and by spectroscopic ellipsometry (SE), from which a growth rate of ~0.3–0.9 Å/cycle is extracted over the 225–275 °C temperature range.

In contrast, there is no ligand exchange observed for the $D_2O$ process within the same temperature range, although some deposition occurs. The deposition rate for the $D_2O$ process calculated by XPS and SE, is ~1.3 Å/cycle within the 225–275 °C window, which is higher than the non-uniform growth rate measured for the ozone process within that temperature range. The higher growth rate and lack of ligand exchange observed with $D_2O$ is tentatively attributed to a CVD component that dominates the film growth process.

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### 11:20am **TF+SE-ThM11 Ultra Fast Compositional Depth Profile Analysis for Microelectronics Applications**

***Agnès Tempez***, Horiba France S.a.s., France, *Y. Mazel, J.-P. Barnes, E. Nolot*, CEA/LETI-University Grenoble Alpes, France, *S. Legendre*, Horiba France S.a.s., France, *M. Chausseau*, HORIBA Instruments Incorporated

Wouldn't it be a considerable gain of time to be able to check the stoichiometry of just deposited thin films in a few minutes? A recently commercially available sputter-based technique called plasma profiling time-of-flight mass spectrometry (PP-TOFMS) is capable to produce, in a few minutes, nm-scale depth resolved profiles of all elements (including light elements) of the periodic table, over a wide dynamic range (from 100% down to ppm)[1]. A simple ratio of the amount of ions detected from a given layer provides a calibration free semi-quantification.

For such fast feedback purposes a PP-TOFMS instrument (Horiba Scientific, Horiba FRANCE SAS, France) has been installed in the clean room of the CEA-LETI in close proximity to process tools.

In this paper we will present data obtained from microelectronics and nanotechnology thin films to demonstrate the performance of the technique. It will be shown that PP-TOFMS can be used for determining composition, detecting contamination, measuring doping level, and characterizing diffusion mechanisms.

For example we will show the ease of detecting, identifying, and locating in depth the presence of unexpected contamination in magnetic Iron Cobalt Boron multi-layers. Another example will show the depth profile of a Germanium Antimony Tellurium alloy deposited on silicon oxide used for phase change memories, a type of non-volatile random access memory. PP-TOFMS depth profiles agree with TOF-SIMS and STEM-EDX analyses for both the first nanometers and the in-depth composition.

[1] A. Tempez et al., J. Vac. Sci. Technol. B (2016) 34

### 11:40am **TF+SE-ThM12 Surface Termination of $Fe_3O_4(111)$ Films Studied by CO Adsorption**

***Francesca Mirabella***, *E. Zaki, F. Ivars, S. Shaikhutdinov, H.-J. Freund*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *X. Li, J. Paier, J. Sauer*, Humboldt Universität zu Berlin, Germany

Although the (111) surface of Fe3O4 (magnetite) has been investigated for more than twenty years, substantial controversy remains in the literature regarding the surface termination [1, 2]. To shed more light on this issue, we performed CO adsorption studies on (111) and (001) oriented thin films, using in-situ infrared reflection absorption spectroscopy, temperature programmed desorption, and scanning tunneling microscopy. The experimental results were rationalized on the basis of theoretical calculations, thus leading to a unified picture in which the $Fe_3O_4(111)$ surface is terminated by 1/4 monolayer of tetrahedrally coordinated $Fe^{3+}$ ions on top of a close-packed oxygen layer as previously determined by low energy electron diffraction. However, surface defects play a crucial role in adsorption properties and most likely dominate chemical reactions on $Fe_3O_4(111)$ when exposed to the ambient.

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# Thin Films Division
# Room: 21 - Session TF-ThM

## Area-selective Deposition and Infiltration Growth Methods
**Moderator:** James Fitz-Gerald, University of Virginia

8:00am **TF-ThM1 Thin-Film Encapsulation Based on ALD Technology for Organic Light-Emitting Diodes**, ***Tony Maindron***, CEA-Leti, France **INVITED**

Thin-film encapsulation of organic electronic circuits like Organic Light-Emitting Diodes (OLED) consists in the addition of vacuum deposited thin mineral barrier directly onto the organic circuit. The main challenge today is to achieve high encapsulation levels with WVTR ~ $10^{-6}$ g/m²/day. The ALD technology is well-suited to reach that goal because the technology allows the deposition of defect-free thin barrier films, mainly of $Al_xO_y$. However, the main limitation of the ALD technology is the relative stability of the $Al_xO_y$ layer when it is exposed to hot humid atmospheres. Due to its high C and H atoms content, resulting from the low temperature deposition used to deposit onto the fragile circuits (maximum process temperature allowed for OLED ~ 100 °C), the $Al_xO_y$ layer corrodes very quickly and loses its barrier properties prematurely. An additional passivation is therefore mandatory in order to protect the $Al_xO_y$ from water condensation onto its surface. Different works have illustrated the benefits of depositing an additional ALD layer on top of the $Al_xO_y$, an additional PECVD or PVD layer on top of the $Al_xO_y$ or using hybrid ALD/MLD ($Al_xO_y$/metalcone) nanocomposites. In each case, the stability of the aluminum oxide is improved because it is not exposed directly to moisture condensation. Alternatively for thin-film encapsulation purposes, other materials of interest can be deposited by low-temperature ALD: $ZrO_2$, $TiO_2$, $SnO_2$, $SiN_x$, ZnO, or ZnO:Al (AZO). After a review of solutions to stabilize $Al_xO_y$ films, performances of new single barrier materials will be described in this work and compare to $Al_xO_y$. It is well-known also that the quality of the encapsulation relies also on the cleanliness of processes. Defects can be described as exogenous particles but they can be seen also as the circuit's surface topography, as well as its surface nature. Getting rid of defects is an important feature for thin-film encapsulation. ALD can provide high surface conformity and can be deposited almost onto every surface. However, as thin-film barriers deposited by ALD remain very thin (dozens of nm), it is mandatory to grow them onto a particle-free surface to ensure a reliable encapsulation. Otherwise, particles can create pinholes that act as a pathway for moisture to reach the fragile device underneath. In the case of OLEDs, black spot features then appear. Other encapsulation processes, based on other deposition technologies like PECVD or PVD, described the use of thick planarization layers to fix the particle issue. Similar strategies can be applied with ALD. The technology developed at CEA-Leti will be presented in the second part of this work.

8:40am **TF-ThM3 Vapor Phase Infiltration: Unifying the Research Community Around Processing Science Fundamentals**, ***Mark Losego***, Georgia Institute of Technology

Vapor phase infiltration (VPI) and its sister processing routes—sequential vapor infiltration (SVI), multiple pulse infiltration (MPI), and sequential infiltration synthesis (SIS)—are exciting, new chemical vapor processing technologies for synthesizing unique organic-inorganic hybrid materials. Because each of these processes were developed independently at various laboratories around the globe and designed to solve different technological problems, a common language has yet to emerge. This lack of a common lexicon introduces unnecessary complexity to the literature and slows the cohesive advancement of the science. This talk seeks to unify the research community around the fundamental science of these processes and demonstrate its uniqueness amongst other chemical vapor processing routes. While VPI/SVI/MPI/SIS emerged from the atomic layer deposition (ALD) research community, its kinetics is substantially different from ALD and truly unique amongst all chemical vapor processes. Unlike ALD and CVD, VPI/SVI/MPI/SIS is not a deposition process but rather an infiltration process composed of three distinct steps: (1) sorption (dissolution) of the gaseous precursor into an organic (polymeric) material, (2) diffusion of that precursor within this host material, (3) entrapment (reaction) of the precursor within the host material (Fig. 1). These unique processing kinetics are similar (identical?) for all of these infiltration processes and rich in fundamental science that intersects with a surprising number of disparate fields including gas membrane separations and solvent vapor annealing. For decades, understanding the fundamental kinetics of ALD and CVD has been the driver for advancing these technologies' processing capabilities; it is now time to do the same for these chemical infiltration processes, such that rationale design physics can be established to devise processing schemes that precisely control the depth and quantity of inorganic infiltration. To guide this unification, this talk will introduce (1) a kinetics-based taxonomy scheme for classifying chemical vapor processes, (2) a basic framework for a common kinetics theory, and (3) a series of common, fundamental scientific questions that, if solved, could significantly advance the utility and expand the use of VPI processing technology.

9:00am **TF-ThM4 Vapor Phase Infiltration (VPI) of Polymers with Intrinsic Microporosity**, ***Emily McGuinness***, *F. Zhang, R.P. Lively, M.D. Losego*, Georgia Institute of Technology

PIM-1, a polymer with intrinsic microporosity, is commonly used for membrane-based chemical separations. However, PIM-1 undergoes detrimental microstructural changes over time and after exposure to certain solvents. In this talk, we will discuss our efforts to use vapor phase infiltration of inorganic components as a means to maintain the microstructure of PIM-1. Vapor phase infiltration (VPI) is a process by which metalorganic precursors are diffused into organic polymer materials to transform them into organic-inorganic hybrids. In this work, we investigate how utilizing VPI can increase PIM-1 durability. We examine VPI of several metal-organic precursors including diethylzinc, trimethylaluminum, and titantium tetrachloride. VPI has been effective in diffusing and trapping inorganic species to a depth of more than 10 microns in PIM-1 material (Figure 1). Gas sorption measurements (BET) indicate that the infiltration process does not significantly decrease the surface area nor the permeability of these PIM-1 membranes (Figure 2). These treatments are also found to improve the chemical stability of PIM-1 when exposed to organic solvents. The kinetics of the VPI process on PIM-1 materials will also be discussed.

9:20am **TF-ThM5 Organic Solvent Resistance of Hybrid Organic-Inorganic Films Synthesized via Vapor Phase Infiltration**, ***Collen Leng***, *M.D. Losego*, Georgia Institute of Technology

We have observed that poly(methyl methacrylate) (PMMA) films infiltrated with trimethylaluminum (TMA) precursors no longer dissolve in toluene, a PMMA solvent. TMA chemically reacting with carbonyl groups in PMMA could be the reason for this solubility resistance. However, films with only a small amount of TMA infiltration will swell significantly inside toluene (over 20% of pre-immersion thickness) and buckle. Interestingly, PMMA films can swell over 50% when infiltrated by TMA at 60 ºC without buckling. We attribute this difference to potential crosslinking of PMMA chains during TMA reactions, resulting in a more rigid film and less polymer chain mobility.

For our experiments, the films are spun-cast on silicon and have thicknesses ranging from around 200 nm to 2 microns. The samples are then treated using VPI, with processing temperatures ranging from 60 to 120 ºC and exposure times ranging from 1 second to full infiltration (on the scale of hours). Spectroscopic ellipsometry is used to track film thickness changes as the treated films are immersed in toluene for times up to several days.

At a processing temperature of 90 ºC, films exposed to TMA for more than 10 minutes no longer dissolve entirely in toluene, but significant film swelling has caused the films to buckle and create micro-folds. Partial delamination of the films from the silicon substrates are also observed due to the buckling actions as well as from small scratches and holes in the films that allow toluene to penetrate and remove the bottom section of the film, where not enough TMA has reacted with PMMA. We find delamination, swelling, and buckling to not be issues for films that are fully treated, which we define as having enough precursor exposure to allow TMA to interact with the entire bulk of the PMMA film. Films that are fully infiltrated remain stable when immersed in toluene for over 10 days.

The results of this study will provide a better understanding of new properties for these polymer films treated by metalorganic precursors. The findings on solubility may be applicable in coatings for various applications.

9:40am **TF-ThM6 Surface Selective CVD of Metallic Thin Films Using Inhibitor Molecules**, ***Elham Mohimi***, *Z. Zhang, S. Liu, B.B. Trinh*, University of Illinois at Urbana-Champaign, *J.L. Mallek*, MIT Lincoln Laboratory, *G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign

In the fabrication of nanoscale devices, the top-down process of lithography and etching is time consuming and expensive. A proposed bottom-up approach – area selective growth – would enable device fabrication beyond conventional patterning limits: thin films would preferentially deposit onto pre-existing portions of a structure with no nucleation and growth on other surfaces. However, a selective process is subject to statistical failure – the nucleation of unwanted material – when it relies on the initial characteristics of the non-growth surface, either the inherent chemical properties or passivation pre-treatments. A robust process requires dynamic control of selectivity to ensure that no stray nucleation occurs on the intended non-growth surfaces for the total time required to deposit film on the device areas.

Here, we present a perfectly selective CVD method which involves adding a neutral molecule "inhibitor" to the process gas mixture: the inhibitor dynamically populates oxide surfaces and prevents nucleation while permitting the deposition of film on metal surfaces, where the inhibitor effect is weaker. Because the inhibitor concentration on the oxide surfaces is continuously replenished, it completely eliminates film nucleation on defects or impurity sites.

We previously demonstrated perfectly selective copper CVD using the Cu(hfac)VTMS precursor with additional VTMS as the inhibitor: no nucleation occurs on thermal $SiO_2$ or on porous, carbon doped oxide, while copper growth occurs on areas covered with a ruthenium seed layer [1]. The excess VTMS scours Cu(hfac) intermediates off the dielectric surface prior to the disproportionation (growth) reaction. Here, we extend the method by using a different class of inhibitor molecules to afford the selective CVD of transition metals and their compounds on a wide variety of oxide substrates; and we explain the mechanism of selectivity .

1. S. Babar, E. Mohimi, B. Trinh, G. S. Girolami and J. R. Abelson, "Surface-selective chemical vapor deposition of copper films through the use of a molecular inhibitor," ECS J. Solid State Sci. Tech. 4(7), N60-63 (2015)

### 11:00am **TF-ThM10 Toward Area Selective Atomic Layer Deposition on Co, W and Ru Metal/Silicon Patterns**, ***Dara Bobb-Semple***, *S.F. Bent*, Stanford University

Modern electronic devices have achieved significantly smaller sizes and increased structural complexity in recent years. Device fabrication today is based on 'top-down' processes with multiple lithography and etching steps which serve as a bottleneck as well as a source of errors for device miniaturization. Area-selective atomic layer deposition (AS-ALD), which combines a surface modification technique and atomic layer deposition (ALD) in a 'bottom-up' approach to nanopatterning,shows great promise in addressing these issues. Most work on AS-ALD typically uses tightly-packed, self-assembled monolayers (SAMs) to modify the substrate surface and block ALD. Past studies have demonstrated AS-ALD on Si/$SiO_2$ substrates patterned with SAMs and, more recently, our group has demonstrated AS-ALD using octadecylphosphonic acid SAMs and alkanethiol SAMs on Cu/$SiO_2$ substrates.

Incorporating the AS-ALD process into any fabrication scheme requires understanding how SAMs interact with different materials. In this work, we have extended our previous studies on Cu substrates to perform comparative studies on the formation of octadecylphosphonic acid and alkanethiol SAMs on three metal substrates: Co, W and Ru. After SAM deposition, model metal (Pt) and metal oxide (ZnO) ALD processes were performed to assess the quality and blocking ability of the SAM layer on the different substrates. X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, X-ray reflectivity, water contact angle (WCA) goniometry, and atomic force microscopy were used to characterize modified samples before and after ALD.

Overall, we observed that the most passivating SAMs of both alkylphosphonic acids and alkanethiols are consistently formed on Co and Ru; SAMs formed on W are less well-packed and hence less reliable in blocking ALD. In fact, XPS results did not show evidence that a SAM was formed on the W substrate following deposition of ODPA in t-butanol, even though increased WCA was observed. Moreover, the solvent was found to play an important role. We found that after a 48h deposition, the Co and Ru substrates passivated using ODPA in t-butanol showed WCA 5° higher on average than when passivated in a toluene solution. Conversely, W substrates showed WCAs < 90° when t-butanol was used as a solvent, but >100° when toluene was used. These results may be explained in terms of the poor Lewis acid character of the W substrate and may indicate a larger role of solvent-substrate interactions in SAM deposition. These studies provide insights that are important for consideration in the development of fabrication processes which incorporate SAMs for AS-ALD.

### 11:20am **TF-ThM11 Area-selective ALD of Ru by Combining an ABC-type ALD Process and $O_2$ Plasma Etching**, *S.N. Chopra, M.F.J. Vos*, Eindhoven University of Technology, The Netherlands, *J.G. Ekerdt*, The University of Texas at Austin, *W.M.M. Kessels*, ***Adrie Mackus***, Eindhoven University of Technology, The Netherlands

Area-selective atomic layer deposition (ALD) is expected to be an enabling technology for the fabrication of future nanoelectronics with sub-10 nm dimensions. In practice it is extremely difficult to achieve high selectivity for area-selective ALD because of undesirable growth initiation on defects and impurities. Given that many processes exist for etching materials, novel combinations of area-selective ALD and etching are currently being considered to eliminate this unwanted growth.[1] In this work, the selectivity of area-selective ALD of Ru on Pt patterns (metal-on-metal deposition) is improved by etching Ru using an $O_2$ plasma after or during the deposition.

ALD of Ru was carried out using an ABC-type process consisting of ethylbenzene-cyclohexadiene Ru(0) precursor, $O_2$ gas, and $H_2$ gas steps. The additional $H_2$ dosing step ensures that metallic Ru is deposited by reducing the $RuO_2$ top layer every cycle. This ABC-type ALD process allows for Ru deposition at low temperatures to exploit the larger differences in growth rates on $SiO_2$ versus Ru or Pt for achieving area-selective ALD. However, even at the low temperature of 150 ºC, for which 500 Ru ALD cycles on Ru resulted in 17.5 nm growth, undesirable Ru islands were observed on the $SiO_2$ non-growth substrate.

When Ru is exposed to $O_3$ or to an $O_2$ plasma, $RuO_4$ is formed as a volatile reaction product. Because $O_2$ plasma has a high selectivity toward Ru etching, it can be used in a post-deposition treatment to eliminate residual Ru islands from the $SiO_2$ non-growth substrate. Area-selective ALD with an almost perfect selectivity was obtained when performing supercycles consisting of Ru ABC cycles and an $O_2$ plasma etch step every 100 cycles. The selectivity of the growth was investigated by performing Ru ALD on Pt-containing seed layers patterned by electron beam induced deposition (EBID) on $SiO_2$ substrates.[2] The $O_2$ plasma etch does not significantly influence the properties of the Ru on the seed layer patterns as will be shown in the presentation.

1. R. Vallat, R. Gassiloud, B. Eychenne, and C. Vallée, *J. Vac. Sci. Technol. A*.**35**, O1B104 (2017)

2. A.J.M. Mackus, S.A.F. Dielissen, J.J.L. Mulders, and W.M.M. Kessels, *Nanoscale* **4**, 4477 (2012).

### 11:40am **TF-ThM12 Enhancing the Inherent Area-selective ALD of $TiO_2$ using $BCl_3$**, ***Seung Keun Song***, *P.C. Lemarie, G.N. Parsons*, North Carolina State University

Area selective deposition of thin film becomes increasingly important as semiconductor industries require shorter node than 10nm scale to alleviate trade-offs between performance and power consumption. Since inherent substrate-dependent selectivity shows relatively narrow selective window, enhancing procedure is required. $TiO_2$ atomic layer deposition (ALD) using titanium tetrachloride ($TiCl_4$) and water has been observed to selectivity deposit $TiO_2$ on Si-OH preferentially over Si-H surfaces. However, the selectivity is lost after initial incubation cycles. In an attempt to better understand selectivity loss mechanisms, we studied the role of surface hydrophobicity and found that the incubation period increased as the contact angle of the initial substrate surface also increased. Furthermore, we incorporated $BCl_3$ into our $TiO_2$ ALD sequence to further enhance the overall selectivity. Through the ellipsometry thickness measurement, $TiO_2$ ALD with $BCl_3$ shows more delayed $TiO_2$ growing on Si-H without delaying on Si-OH. Using quartz crystal microbalance (QCM) we show that $BCl_3$ appears to impede $TiO_2$ growth, rather than significantly etching $TiO_2$. Finally, we provide evidence that the ability to effectively impede $TiO_2$ deposition on Si-H without significantly reducing deposition on the Si-OH surface depends on the amount and frequency of $BCl_3$ dosing. This work ensures better selectivity than previous result.

### 12:00pm **TF-ThM13 Selective ALD by Intercalation of Etching Cycles in PEALD Process**, ***Rémi Vallat***, *R. Gassilloud*, CEA/LETI-University Grenoble Alpes, France, *C. Vallée*, Université Grenoble Alpes & CEA, LETI, Minatec Campus, Grenoble, France

Therefore complementary techniques are needed to continue extreme scaling and extend Moore's law. Selective deposition processes can be used to increase and enhance patterning capabilities at very low cost. In our lab, a new selective Plasma Enhanced ALD process has been developed by adding etching steps in the PEALD flow. To be effective, 3 conditions must be satisfied (Figure 1):

- A different nucleation delay on different substrates
- A nm scale etching of the thin film
- The etching step must add a new nucleation delay

We used this process for the selective deposition of $Ta_2O_5$ with TBTDET (TertButylimido Tris(DiEthylamino Tantalum) precursor and a plasma gas mixture of $O_2/Ar/NF_3$ for deposition and etching steps. $Ta_2O_5$ has been selectively deposited on a metal substrate (TiN) versus $SiO_2$ and Si substrates (no deposition on these substrates). For this process, the different substrates have been patched onto a Si wafer and introduced simultaneous into the PEALD reactor. [1]

For this presentation we will present the selective process developed for $TiO_2$ with TDEAT (Tetrakis DiEthylAmido Titanium) precursor. The ALD selective process has been successfully developed for the deposition of $TiO_2$ on three different metallic substrates (TiN, NiPt and W). As for $Ta_2O_5$ deposition, a thin $TiO_2$ film is deposited on the different metal substrates but not on Si and $SiO_2$ substrates although all substrates are introduced simultaneously in the deposited chamber. Details on the process will be given during the presentation with a focus study on precursors and radicals interactions with the different surfaces after each step of the process. In this study, quasi in situ XPS was used. Figure 2 shows Ti*2p* peak for one titanium pulse on silicon substrate with or without etching step. Fluorine treatment lead to thinner layer. This difference is explained by Si-F and Si-O-F bonds presence at the surface. This fluorine bonds blocks the titanium growth.

The thin oxide films selectively deposited will be used in 3D nonvolatile memory devices. Our objective is to realize a crosspoint memory in backend level from a pattern area or a trench area without the photolithography step. Therefore, electrical properties of the $Ta_2O_5$ and $TiO_2$ oxides deposited with the standard PEALD process are compared to those of thin films selectively deposited thanks to C(V), C(f) and I(V) measurements. We will show that the selective ALD process does not degrade the dielectric properties of the films in terms of leakage current and electrical field breakdown. Resistive memories cycles are also compared and discussed. Finally, 3D structures with the selective deposition process will be shown.

## Tribology Focus Topic
## Room: 10 - Session TR+AC+TF+VT-ThM

### Lubricant, Coatings, and Biotribology
### **Moderator:** J. David Schall, Oakland University

8:00am **TR+AC+TF+VT-ThM1 Superlubricity of Hard Compliant Carbon Coatings with Green Lubricants: Role of Surface Chemistry and Structural Changes**, ***Maria-Isabel De Barros Bouchet***, Ecole Centrale de Lyon - LTDS, France **INVITED**

Reduction of energy loss by mechanical friction has been strongly required in recent years for improving fuel efficiency especially for automotive engine. Even at a modest rate, it is of primary importance to reduce parasitic energy losses and provide environmental sustainability. An approach to achieve this target is the development of new lubrication technologies, combining new lubricant formulations and cutting-edge coatings transferable to industrial applications. Since superhard carbon material like tetrahedral amorphous carbon (ta-C) and Nano-Crystalline Diamond (NCD) coatings combine both crucial properties, high hardness with an ultra-smooth surface roughness, they have attracted a growing interest in the last decade. While the friction coefficient is generally extremely high under ultra high vacuum conditions, in the earlier years we have discovered the ability of these coatings to be lubricated by selected biodegradables green molecules like fatty acids, glycerol mono-oleate GMO and polyols, as well as their mixture with synthetic base oil such as Poly-Alpha Olefines (PAO). Some of these compounds are able to lubricate ta-C and NCD coatings with a friction coefficient below 0.01 (so-called superlubricity) in thin-film EHL/mixed regime and below 0.03 in severe boundary regime without significant wear1. As this case of superlow friction is extremely promising for many applications fields, the related mechanism has been investigated and a special attention has been paid to the surface chemistry and structural changes of the carbon coatings. By coupling advanced extreme surface analyses (PES and XANES), we show that the mechanism of friction reduction is related to the tribo-formation of quasi-2D planar graphene-like structures at the top of the colliding asperities (thickness about 1 nm). Eventually, the graphene can be slightly oxidized by the OH-groups coming from the tribo-decomposition of the lubricant molecules trapped between asperities. Moreover, the rubbed sub-surface is enriched with sp2-hybridized carbon, such as in a soft a-C material, during the friction2. These strong structural changes certainly ease the tribochemical-formation of the carbon rings present in the graphene-like structure as pointed out by atomistic computer simulations.

1. M. Kano, J. M. Martin, K. Yoshida, M.I. De Barros Bouchet, Friction J., 2 (2) (2014) 156.

2. M.I. De Barros Bouchet, J.M. Martin, J. Avila, M. Kano, K. Yoshida, T. Tsuruda, S. Bai, Y. Higuchi, N.i Ozawa, M. Kubo and M. C. Asensio, Scientific Reports, 2017 (DOI: 10.1038/srep46394).

8:40am **TR+AC+TF+VT-ThM3 Role of Deuterium and Hydrogen in the Physical Understanding of Nano-friction in a-C:H/D Thin Films**, *F.G. Echeverrigaray, S.R. Sales de Mello, A.F. Michels,* UCS, Brazil, *F. Alvarez,* UNICAMP, Brazil, ***Carlos Figueroa***, UCS, Brazil

The friction phenomenon is a complex manifestation of the nature. In spite of phenomenological laws can describe the friction force at different scales, the fundamental physical understandings of such a phenomenon do not have consensus. Phenomena such as phononic, electronic, magnetic, and also electrostatic effects and models were developed in order to explain the meta- and nano-friction behavior of materials. In this work, we report the friction behavior of a diamond spherical dome sliding on different amorphous carbon thin films containing different amounts of hydrogen and/or deuterium inspecting at the meta-nanoscale indentation. Two important situation are reported. Firstly, for samples where hydrogen was replaced by deuterium in the thin film bulk, the friction coefficient decreases for increasing *deuterium* included in the carbon underneath structure. Secondly, for samples where hydrogen content is increased on the surface, the friction coefficient decreases with the increasing of the ratio H/C at the surface. In this paper, we discuss two different physical mechanisms describing these peculiar experimental results: dissipation effects associated with phonon coupling and van der Waals forces contributions coexisting and determining the friction behaviour of a-C:H/D for the cited studied situations.

9:00am **TR+AC+TF+VT-ThM4 Imaging X-Ray Absorption Spectroscopic Investigation of the Mechanisms Behind the Environmental Dependence of the Tribological Properties of Amorphous Carbon Surfaces**, ***Filippo Mangolini***, University of Leeds, UK, *M. Koshigan,* Ecole Polytechnique Montréal, Canada, *M.H. Van Benthem, J.A. Ohlhausen,* Sandia National Laboratories, *J.B. McClimon, J. Hilbert,* University of Pennsylvania, *J. Fontaine,* Ecole Centrale de Lyon, France, *R.W. Carpick*, University of Pennsylvania

Among the variants of diamond-like carbon films developed for the ever-increasing performance and durability requirements of tribo-mechanical applications, silicon oxide-containing hydrogenated amorphous carbon (a-C:H:Si:O) is of interest as it exhibits good tribological performance across a broader range of environments compared to hydrogenated amorphous carbon, and higher thermo-oxidative stability. However, the scientific basis for this improved behavior is not established. In this work, we develop a fundamental understanding of the structural transformations occurring in a-C:H:Si:O when sliding against steel in different environments (from high vacuum to controlled hydrogen and oxygen pressures). The results of tribological experiments revealed that upon increasing the oxygen pressure in the experimental chamber from 10 mbar to 1000 mbar, the coefficient of friction increased from 0.02±0.01 to 0.06±0.01, whereas upon increasing the hydrogen pressure from 50 mbar to 2000 mbar, the coefficient of friction decreased from 0.08±0.01 to 0.02±0.01.The subsequent near edge X-ray absorption fine structure (NEXAFS) spectroscopic measurements and X-ray photoelectron spectroscopy (XPS) analyses provided insights into the structural transformations and chemical reactions occurring in a-C:H:Si:O upon sliding. Independently of the gas, a stress-induced conversion from sp$^3$- to sp$^2$-bonded (disordered) C-C bonds occurs. When sliding in hydrogen, the newly-generated, strained sp$^2$ carbon layer reacts with hydrogen molecules to form a hydrogenated amorphous carbon interfacial material. Upon increasing the hydrogen pressure, the fraction of C-H bonds increases in the near-surface region of the wear tracks formed on a-C:H:Si:O. This is proposed to progressively lower the shear strength of the material at the sliding interface, thus resulting in a decrease of friction with hydrogen pressure. When sliding in oxygen, the dissociative reaction of oxygen molecules with strained sp$^2$ C-C bonds leads to the formation of C=O groups. Additionally, increasing the oxygen pressure during tribological testing leads to an increase in oxygen concentration in the near-surface region of a-C:H:Si:O together with an increase in the fraction of Si atoms in high oxidation states. These surface chemical changes and structural transformations are proposed to increase friction with oxygen pressure by progressively increasing the shear strength of the material generated at the sliding interface.

9:20am **TR+AC+TF+VT-ThM5 Structure Evolution in Tribological Interfaces Studied by Multilayer Model Alloys**, ***Martin Dienwiebel***, *E. Cihan*, Karlsruhe Institute for Technology (KIT), Germany **INVITED**

During sliding of surfaces the near surfaces undergo significant changes in terms of topography, composition and microstructure and a so-called "third body" or "tribomaterial" forms which differs strongly from the bulk materials in terms of topography, composition and microstructure. Initially we use multilayer model alloys of an Au/Ni layer system to study effects of grain size on steady-stady friction by varying the layer spacing and the number of layers. Experiments are performed in a UHV microtribometer, the analysis of microstructure before and after tribological stressing is done by FIB and STEM and the chemistry is investigated by XPS.During sliding of surfaces the near surfaces undergo significant changes in terms of topography, composition and microstructure and a so-called "third body" or "tribomaterial" forms which differs strongly from the bulk materials in terms of topography, composition and microstructure. Initially we use multilayer model alloys of an Au/Ni layer system to study effects of grain size on steady-stady friction by varying the layer spacing and the number of layers. Experiments are performed in a UHV microtribometer, the analysis of microstructure before and after tribological stressing is done by FIB and STEM and the chemistry is investigated by XPS.

11:00am **TR+AC+TF+VT-ThM10 Carbon, Carbon Everywhere, from Catalysts to Hip Implants**, ***Laurence Marks***, Northwestern University **INVITED**

Friction is a pervasive problem, by some estimates consuming about 5% of the GDP of the economies of the developed world, and a recent analysis has indicated that about one third of the fuel energy in automobiles goes to overcoming frictional losses. While the importance of minimizing friction can be traced back at least as far as the tomb of Tehuti-Hetep, circa 1880 B.C, where a man can be seen pouring a lubricant to assist moving a statue, there are still many unknowns in the field of tribology which encompasses friction as well as other critical processes such as wear and lubrication. For many of the phenomena in tribology there are still numerous unknowns. When it comes to biological systems most work to date has assumed that different mechanisms are taking place than occur for inorganic systems. While there are differences, there are also significant similarities particularly in implants when inorganic and biological meet. We have recently shown that for metal implants in-vivo the same type of graphitic materials that appear in many areas ranging from heterogeneous catalysis to oil lubrication are present. Beyond just lubrication, corrosion of these materials is not special to biological systems, but has strong similarities to established factors such as grain boundary precipitation and a significant role for molybdenum as reducing the occurence of breakdown of the protective oxide film via complex processes involving solute trapping. These and related recent results will be described.

11:40am **TR+AC+TF+VT-ThM12 Tribology of Cellular Interfaces**, ***Angela Pitenis****, J.M. Urueña, S.M. Hart, T.T. Hormel, C.S. O'Bryan, S.L. Marshall, K.D. Schulze, P.P. Levings, T.E. Angelini, W.G. Sawyer*, University of Florida **INVITED**

Human health, mobility, and quality of life critically hinge on the body's ability to provide adequate lubrication between most contacting and sliding biological interfaces. Soft, aqueous, and mucinated biopolymer networks lining all moist epithelia enable the body to provide lubricity over a wide range of contact pressures and sliding speeds. The exquisite slipperiness and softness of biological sliding interfaces present significant experimental challenges for fundamental studies on their tribological performance. Physiological contact pressure conditions must be matched in in vivo, ex vivo, and in vitro studies that aim to acquire physiologically-relevant friction measurements. While biotribological investigations using living cells, cell layers, and tissues necessitate low contact pressure measurements, such studies frequently rely on the application of low forces to achieve accomodating contact pressures (kPa range), and traditional methods can decrease the contact area below a physiologically-relevant threshold. The softness of a cell layer (E ~ 10 kPa) provides an order-of-magnitude estimate for the amount of mechanical pressure that may be applied to cells during tribological testing; contact pressures about 5 kPa and shear stresses in excess of 200 Pa are sufficient to wreak significant damage to a cell layer. Recently, direct contact tribological experiments on a living cell layer without incurring any measurable cell death in the sliding path has become possible through the application of a soft, thin, spherically-capped membrane hydrogel probe. With this experimental configuration, in vitro tribological experiments were performed against a monolayer of mucin-producing human corneal epithelial cells (hTCEpi) for 10,000 reciprocating cycles at physiologically-relevant contact pressures and challenging sliding speeds. The gel-cell sliding interface under applied normal loads of ~ 200 µN resulted in measured friction coefficients of µ ~ 0.06 and achieved shear stresses on the order of 60 Pa, which is below the critical shear stress for inducing cell death; excellent cell survival rates (~99.8%) were measured after extended duration tribological experimentation.

## 2D Materials Focus Topic
## Room: 15 - Session 2D+AS+SS-ThA

## Dopants, Defects, and Interfaces in 2D Materials
**Moderator:** Aubrey Hanbicki, Naval Research Laboratory

2:20pm **2D+AS+SS-ThA1 Electron Irradiation-induced Defects and Phase Transformations in Two-dimensional Inorganic Materials**, ***Arkady Krasheninnikov***, Helmholtz Zentrum Dresden-Rossendorf, Germany

Following isolation of a single sheet of graphene, many other 2D systems such as hexagonal BN, transition metal dichalcogenides (TMDs) and silica bilayers were manufactured. All these systems contain defects and impurities, which may govern the electronic and optical properties of these materials, calling upon the studies on defect properties. In my talk, I will present the results [1-6] of our first-principles theoretical studies of defects (native and irradiation-induced) in inorganic 2D systems obtained in collaboration with several experimental groups. I will further dwell on the signatures of defects in Raman spectra and discuss defect- and impurity-mediated engineering of the electronic structure of inorganic 2D materials. I will also present the results [7] of our theoretical studies of electron-beam induced phase transformations in 2D TMDs when electric charge, mechanical strain and vacancies are present. Based on the results of our calculations, we propose an explanation for this phenomenon which is likely promoted by charge redistribution in the TMD monolayer combined with vacancy formation due to electron beam and associated mechanical strain in the sample.

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2:40pm **2D+AS+SS-ThA2 Key Role of Rotated Domains in Oxygen Intercalation at Graphene on Ni(111)**, ***Luca Bignardi***, *P. Lacovig, M. Dalmiglio,* Elettra-Sincrotrone Trieste, Italy, *F. Orlando,* Paul Scherrer Institut (PSI), Switzerland, *A. Ghafari,* Helmholtz-Zentrum Berlin, Germany, *L. Petaccia,* Elettra-Sincrotrone Trieste, Italy, *A. Baraldi,* University of Trieste, Italy, *R. Larciprete,* Istituto dei Sistemi Complessi - CNR, Italy, *S. Lizzit*, Elettra-Sincrotrone Trieste, Italy

In this contribution I will provide a description of the oxygen intercalation at the strongly interacting graphene on Ni(111) and of the role of rotated graphene domains in triggering the intercalation. The system was studied by a combination of high-resolution x-ray photoelectron spectroscopy (HR-XPS), photoelectron diffraction (XPD) and angle-resolved photoemission (ARUPS) performed with synchrotron radiation. The HR-XPS measurements provided a full characterization of the interface at each stage of the intercalation, revealing the formation of an oxide layer between graphene and the metal substrate. The ARUPS data showed that the oxide layer efficiently decouples graphene from the substrate, restoring the Dirac cone and providing a slight n-doping. The C1s XPD measurements revealed that the graphene domains not aligned with the Ni substrate are the first to be intercalated with oxygen. At the same time, these domains are also preferential regions under which the oxygen is retained during the deintercalation process.

3:00pm **2D+AS+SS-ThA3 Atomic Structure of Defect and Dopants in 2D Semiconductor Monolayer $MoS_2$ and $WS_2$**, ***Jamie Warner***, University of Oxford, UK **INVITED**

Defects impact the properties of materials and understanding their atomic structure is critical to their interpretation and behaviour. I will discuss how aberration corrected TEM can be used to resolve the detailed structure of Sulfur vacancies and grain boundaries in CVD grown MoS2 and WS2. I will present our latest results on detecting single Cr and V impurity dopants that substitute Mo and W sites. Electron energy loss spectroscopy is used to map out the spatial position and confirm the contrast profiles from HAADF STEM images. Single Pt atimsnare added to the surface of MoS2 and we study the dynamics of hopping between S vacancies. finally I will discuss in situ observations of Pt nanocrystal formation on MoS2 using high temperature annealing.

4:00pm **2D+AS+SS-ThA6 Interaction of an Energetic Ar Molecular Cluster Beam with Graphene**, ***Songkil Kim***, *A.V. Ievlev, J. Jakowski, I. Vlassiouk, M.J. Burch, C.C. Brown, A. Belianinov, B.G. Sumpter, S. Jesse, O.S. Ovchinnikova*, Oak Ridge National Laboratory

Manipulation of low dimensional nanomaterials provides intriguing opportunities to design new functional materials as well as to develop next-generation device applications. To manipulate properties of low dimensional nanomaterials, extensive study has been conducted so far for interaction of energetic particles with low dimensional nanomaterials. However, most of the research has been focused on utilizing electron or light/heavy ion beams to study irradiation effects on alternation of structural, mechanical and electrical properties of nanomaterials. In this study, we investigated the effect of Argon molecular cluster beam irradiation on both defect formation and removal of organic contaminants on graphene. An Argon cluster beam was generated using the Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) combined with Atomic Force Microscopy (AFM). The ToF-SIMS allows for conducting in-situ monitoring of defect formation as well as organic contaminants removal. This leads to accomplishments of a high degree of controls over modification of graphene. A systematic study has been conducted to provide in-depth understanding about defect formation of graphene by synergistic theoretical and experimental approaches. Raman spectra clearly indicate that suspended graphene is more susceptible to Ar cluster beam irradiation than supported graphene on a $SiO_2$/Si substrate under the same irradiation conditions. The underlying mechanisms for the experimentally observed phenomena are demonstrated by theoretical analysis using the first-principles molecular dynamics calculations.

This work was supported by the Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy, Office of Science User Facility.

4:20pm **2D+AS+SS-ThA7 Efficient and Low-Damage N-doping of Graphene by Nitrogen Late-Afterglow Plasma Treatment**, ***Xavier Glad***, *G. Robert-Bigras, P. Levesque, R. Martel, L. Stafford*, Université de Montréal, Canada

Graphene already shows promises for the next generation of electronics and optoelectronics devices and other applications where a band gap or magnetic response is necessary [1]. The availability of versatile processing techniques is thus crucial to the development of these graphene-based technologies. An ideal and efficient nitrogen doping would precisely tune the N-doping and keep a minimal defect density. In this work, we explore the potential of the late afterglow of a microwave $N_2$ plasma at reduced pressure (6 Torr) for post-growth tuning of CVD-grown graphene films on copper foils.

A single graphene sample received five subsequent 30-second plasma treatments between which X-Ray photoelectron spectroscopy (XPS) and Raman spectroscopy (RS) were carried out. XPS measurements confirmed a strong N-incorporation increasing with the plasma treatment time (up to N/C = 29%) while RS assessed an uncommonly low damage generation (D/G ratio below 0.4) for such incorporation.

XPS, RS and ultraviolet photoelectron spectroscopy (UPS) were also performed on the sample after transfer to an Si/$SiO_2$ substrate via the PMMA method [2]. The results show a strong decrease of the N content (N/C = 6%) which is attributed to the desorption of out-of-plane adsorbed N due to the transfer. RS and UPS techniques both support an n-doping which is associated to the different aromatic N-incorporations deconvoluted from the high resolution XPS spectra.

The low ion density ($< 10^7$ cm$^{-3}$) and the high density of reactive neutral ($> 10^{14}$ cm$^{-3}$) and metastable species ($> 10^{10}$ cm$^{-3}$) of the nitrogen late-afterglow in our conditions [3] are believed to be the key of such efficient and low-defect N-incorporation in graphene.

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4:40pm **2D+AS+SS-ThA8 Exploring the Electronic Signature of Disordered Monolayer $MoS_2$**, ***Chinedu Ekuma***, *D. Gunlycke*, Naval Research Laboratory

Atomic defects in two-dimensional semiconductors could be used to induce insulator-metal- transitions (IMT), making it possible to have both insulating and metallic behavior in different regions of a single seamless material. Using a first-principles-based many-body typical medium dynamical cluster approach [1], we explore the electronic signature in monolayer $MoS_2$ resulting from atomic defects. Analyzing the typical (geometric) density of states, which unlike the arithmetic density of states, is able to discern localized and delocalized states, our calculations show a correlation-mediated IMT at the experimentally relevant sulfur vacancy concentration ~$10^{13}$ $cm^{-2}$, depending on the strength of the intrinsic electron-electron interactions. We will also discuss the role of atomic defects on the absorption spectra.

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Acknowledgements: This work has been funded by the Office of Naval Research (ONR), directly and through the Naval Research Laboratory (NRL). C.E.E. acknowledges support through the NRC Research Associateship Programs.

5:00pm **2D+AS+SS-ThA9 Heterogeneity in 2D Materials: From Localized Defects, Isoelectronic Doping to Macroscopic Heterostructures**, ***Kai Xiao***, *X. Li, M. Mahjouri-Samani, M.-W. Lin, L. Liang, A. Oyedele,* Oak Ridge National Laboratory, *M. Tian,* University of Tennessee, *A.A. Puretzky, J. Idrobe, M. Yoon, B.G. Sumpter,* Oak Ridge National Laboratory, *G. Duscher,* University of Tennessee, *C.M. Rouleau, D.B. Geohegan*, Oak Ridge National Laboratory **INVITED**

Two-dimensional (2D) materials are intrinsically heterogeneous, therefore controlling defects, understanding the impact of boundaries and interfaces, and developing means to exploit these heterogeneities is a transformative opportunity that could underpin future technologies and energy applications. This talk will discuss the fundamental understanding of the roles of heterogeneity, atomic interface, and disorder in 2D materials and their heterostructures. Through isoelectronic doping in monolayer of $MoSe_2$, the Se vacancies are effectively suppressed and photoluminescence is significantly enhanced due to the decrease of defect-mediated non-radiative recombination. In addition, we demonstrate the non-equilibrium, bottom-up synthesis of single crystalline monolayers of 2D $MoSe_{2-x}$ with controllable levels of Se vacancies far beyond intrinsic levels. Both substitutional dopants and vacancies were shown to significantly alter the carrier properties and transport characteristics within a single monolayer (e.g., n- to p-type conduction in W-doped $MoSe_2$ and in Se-deficient $MoSe_{2-x}$). The vertical and lateral 2D heterostructures by controlled assembly and doping will be discussed. In addition, the lattice misfit heterostructures of monolayer GaSe/$MoSe_2$ were synthesized by a two-step chemical vapor deposition (CVD) method. We find the vertically stacked GaSe/$MoSe_2$ heterostructures maintain vdW epitaxy with well-aligned lattice orientation between the two layers, forming an incommensurate moiré superlattice. The bottom up synthesis of 2D materials discussed here provides excellent control over the heterogeneity in 2D materials, which can tunably modulate the optical and electrical properties in 2D materials and their heterostructure.

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

5:40pm **2D+AS+SS-ThA11 Evidence of a One-dimensional Metal in Twin-grain Boundaries of $MoSe_2$**, ***Horacio Coy Diaz***, *M. Batzill*, University of South Florida

In monolayer van der Waals-materials, grain boundaries become one-dimensional (1D) line defects. Here we show using angle resolved photoemission spectroscopy (ARPES) that twin-grain boundaries in the 2D semiconductor $MoSe_2$ exhibit parabolic metallic bands. The 1D nature is evident from a charge density wave transition, whose periodicity is given by $k_F/p$, where the Fermi momentum $k_F$ is determined by ARPES. Most importantly, we provide evidence for spin- and charge-separation, the hallmark of 1D quantum liquids. ARPES shows that the spectral line splits into distinctive spinon and holon excitations whose dispersions exactly follow the energy-momentum dependence calculated by 1D Hubbard model, with suitable finite-range interactions. Our results also imply that quantum wires and junctions can be isolated in line defects in 2D materials, which may enable quantum transport measurements and devices.

## Applied Surface Science Division
## Room: 13 - Session AS+SS-ThA

## Advances in Instrumentation and Data Analysis

**Moderators:** Thomas Grehl, ION-TOF GmbH, Germany, Bonnie June Tyler, Universität Münster

2:20pm **AS+SS-ThA1 Submicron Spot Sampling Resolution in Thermal Desorption Atomic Force Microscopy - Mass Spectrometry Via Rapid Heating Functions**, *S. Somnath, S. Jesse,* ***Gary Van Berkel***, *S.V. Kalinin, O.S. Ovchinnikova*, Oak Ridge National Laboratory

Atomic Force Microscopy (AFM) combined with Mass Spectrometry (MS) can provide the ability to map and correlate the molecular and physical properties of samples at sub-micron resolutions. One such hybrid system employs heated AFM probe for thermal desorption (TD) sampling of molecules from a surface and subsequent gas phase ionization and detection of the liberated species by MS. However, current heating techniques typically result in a minimum spot size of 1-2 µm for most real-world samples where the where the melting and vaporization points are further apart since the majority of the thermal energy from the thermal probe only melts or damages the substrate. While substantial research in the past has focused on improving the instrumentation, the waveforms used for heating thermal probes have been ignored. Heated AFM probes are capable self-heating at rates approaching 1E+9 K/s to reach temperatures in excess of 1300 K. Prior research has shown that increasing the heating rate (> 1E+9 K/s) can enable thermal desorption of intact molecules off the sample surface.

Here, we report on the use of voltage pulse trains to tailor probe heating such that spot sampling size was reduced and desorption efficiency (DE), defined as the ratio of the mass spectral signal to the volume of the desorption crater, was improved compared to the conventional heating method. We developed a 1D finite element joule-heating model of the probe-sample system that predicted the cantilever response to different heating functions, to guide the development and optimization of the heating functions and aid in interpreting experimental results. Using a model system composed of a thin film of ink containing pigment yellow 74 as a model system, desorption craters shrunk from 2 µm, using the conventional approach, to 310 nm using the optimum tailored heating function. This same pulsed heating function produced a 381× improvement in the DE and an 8× improvement in spatial resolution compared to the conventional heating approach showing that signal/amount of material sampled was improved significantly by this new probe heating strategy.

3:00pm **AS+SS-ThA3 Data Analysis in Thin Film Characterization: Learning More With Physical Models**, ***Lev Gelb***, *A.V. Walker*, University of Texas at Dallas **INVITED**

Chemical imaging methods, including imaging mass spectrometry (MS), are increasingly used for the analysis of samples ranging from biological tissues to electronic devices. Most chemical analyses for advanced materials, nanosystems, and thin films involve energetic beams of primary ions or electrons. These unavoidably cause chemical damage, including surface roughening, which confuses data interpretation. In secondary ion mass spectrometry (SIMS) matrix effects can be significant, in which the signal obtained from a given species may change depending on its surroundings. All these phenomena lead to the same issue: the data measured are not necessarily representative of the elements or species originally present, or their original locations. These effects can sometimes be exploited to provide new information or increased sensitivity, as in matrix-enhanced SIMS and the determination of overlayer thicknesses from attenuation of XPS substrate intensity.

We discuss analysis of such data using maximum *a posteriori* (MAP) reconstruction based on physically motivated models, and contrast this approach with statistical dimensionality-reduction techniques such as Principal Components Analysis. We present progress towards the quantitative extraction of chemical concentration profiles, component spectra, sample topography and other information from imaging mass spectrometry data in the presence of matrix effects. These include systems that demonstrate "weak" matrix effects, such as mixed self-assembled monolayers, and “strong” matrix effects such as those observed in ionic liquid matrix enhanced secondary ion mass spectrometry.

We also draw comparisons with related nonlinearities in other analysis methods, in particular X-ray photoelectron spectroscopy (XPS). While XPS is often considered to have linear response with concentration, this is only true under certain conditions and does not necessarily apply in sputter-based depth profiling experiments. We discuss extension of the MAP approach to such experiments and point out similarities with its application to SIMS data.

4:00pm **AS+SS-ThA6 Advanced Analysis of XPS and ToF-SIMS Data**, ***Matthew Linford***, *S. Chatterjee*, *B. Singh*, Brigham Young University, *N. Gallagher*, Eigenvector Inc., *M.H. Engelhard*, EMSL, Pacific Northwest National Laboratory **INVITED**

Surface analysis plays a critical role in many areas of science and industry, and X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) are much used analytical techniques that provide information about the outermost layers of materials. In this presentation, I discuss the application of multivariate spectral techniques, including principal component analysis (PCA) and multivariate curve resolution (MCR), to the analysis of XPS and ToF-SIMS depth profiles. Multivariate analyses often provide insight into data sets that is not easily obtained in a univariate fashion. The information content (IC) or entropy, which is based on Shannon's information theory, is also introduced. This approach is not the same as the mutual information/entropy approaches sometimes used in data processing. A discussion of the theory of each technique is presented. PCA, MCR, and IC are applied to four different data sets obtained via a ToF-SIMS depth profile through ca. 100 nm of $C_3F_6$ on Si, a ToF-SIMS depth profile through ca. 100 nm of PNIPAM (poly (N-isopropylacrylamide)) on Si, an XPS depth profile through a film of $SiO_2$ on Si, and an XPS depth profile through a film of $Ta_2O_5$ on Ta. PCA, MCR, and IC reveal the presence of interfaces in the films, and often indicate that the first few scans in the depth profiles are different from those that follow. Both IC and backward difference IC analysis provide this information in a straightforward fashion. Rises in the IC signal at interfaces suggest greater complexity to scans from interfaces in depth profiles. Results from PCA were often rather difficult to understand owing to the complexity of its scores and loadings plots. MCR analyses were generally more interpretable.

4:40pm **AS+SS-ThA8 Using the Auger D-Parameter to Identify Polyatomic Molecular Species**, ***Sabrina Tardio***, *P.J. Cumpson*, NEXUS, Newcastle University, UK

When analysing organic materials using XPS, the interpretation of the C1s spectra can be quite challenging and particularly difficult is to distinguish between unsaturated/aromatic carbon (hybridised sp2) and aliphatic carbon (hybridised sp3). This is because their binding energies of the two are very close and, in some cases, overlap or even invert the expected trend. This problem can be approached by observing the C*KLL* auger peak of the XPS spectra that is present around 260 eV of kinetic energy. Historically, information on the C sp2/sp3 ratio is obtained by analysing the width of this, extracting a metric commonly known as the D-Parameter. This is calculated by taking the first derivative of the auger feature and measuring the distance (in eV) between the position of the maximum (the most positive) and the minimum (the most negative) peaks observable. It was shown that there is a linear correlation between the D-Parameter with sp2 hybridised carbon content in a surface. For example, graphite (100% sp2 character) has a D-Parameter around 22eV while diamond (100% sp3 character) has a D-Parameter around 13eV. The D-Parameter is widely used for the identification of carbon allotropes; graphite, graphene, amorphous, diamond like carbon (DLC) diamond, hydrogenated diamond etc. However, the metric has found little or no use for the identification of unsaturated and saturated carbon in polymers or, more generally, polyatomic molecules. Although the principle remains the same; the correlation between D-parameter and sp2 carbon is still true, the presence of hydrogen as well as other atoms other than carbon, makes the relationship between the two much more complex. In this work correlations of the D-parameter with the C Sp2/sp3 ratio, the ratio between hydrogen bonded to C sp2 and sp3 and the ratio between heteroatoms (such as oxygen) bonded to sp2 and sp3 carbons is shown. In particular, a linear relationship between a combination of these ratios and the d-parameter was found. This allows one to predict the d-parameter for a given organic compound as well as to obtain more information about unknown species analysed. It will be shown how the combination of different information obtained from XPS spectra: photoelectron high-resolution peaks (C1s O1s), valence band and D-Parameter can lead to a quite accurate identification of organic molecules.

5:00pm **AS+SS-ThA9 XPS Analysis of Multilayer $HfO_2$ Using Hard and Soft X-rays**, ***Jennifer Mann***, Physical Electronics, *R. Inoue*, *H. Yamazui*, *K. Watanabe*, ULVAC-PHI, Japan, *J. Newman*, Physical Electronics

Hard x-rays can generally be considered as having photon energies > 5 keV, while photon energies below 5 keV are described as soft x-rays. Hard x-ray photoelectron spectroscopy (HAXPS) is typically performed at large synchrotron facilities, while most commercial lab-scale XPS instruments use soft x-rays. The PHI *Quantes* is a new commercial laboratory instrument equipped with two scanning microprobe, monochromated x-ray sources, Cr $K_\alpha$ (5414.9 eV) and Al $K_\alpha$ (1486.6 eV). Use of higher photon energies increases the mean free path of photoelectrons, resulting in an increased information depth obtained from the sample (~3x that of Al $K_\alpha$). HAXPS measurements are therefore more sensitive to the bulk and contributions from the surface are minimized [1,2]. Toggling between x-ray sources allows non-destructive depth analysis of multilayer thin films and buried interfaces [1]. A more detailed description of the instrument will be presented in reference [3].

Initial analysis results on the high-k dielectric, $HfO_2$, obtained on the PHI *Quantes* using both hard and soft x-ray sources will be presented. Several samples of $HfO_2$ on $SiO_2$ on Si substrate with varying thicknesses of the $HfO_2$ and $SiO_2$ layers were analyzed. The $HfO_2/SiO_2$ thicknesses of the samples are as follows: 27Å/28Å, 80Å/22Å, 81Å/81Å and 263Å/22Å. Spectra were collected with a 90 degree take-off angle to maximize the information depth of each sample. As expected, the presence and relative intensities of $SiO_2$ and Si substrate peaks varied depending on the sample thickness, photon energy and photoelectron kinetic energy.

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5:20pm **AS+SS-ThA10 Novel Systems Toward Ambient Pressure Photoemission Spectroscopy**, ***Lukasz Walczak***, PREVAC, Poland

Nowadays, he complexity of materials and their surfaces is expanded across a wide range of topics, including surface science, catalysis, corrosion, photoelectrochemical energy conversion, battery technology, or energy-saving technologies [1-6]. An unique and exceedingly flexible analysis cluster with a detection system is needed for this applied research. Here the examples of innovative, compact ambient pressure X-ray spectroscopy systems with a some experimental results. One of the example will be a laboratory based high pressure x-ray photoelectron spectroscopy (HPXPS). The focus is on the usability of the system for various types of studies relevant for high level research for photo-catalytic reactions, light harvesting and solar cell development [6]. Further examples will be the advanced HP cell with the ambient pressure X ray spectroscopy system and flexible gas inlet system to allow for frontier research on gas-solid interactions. Systems are equipped with the possibility of process automatization in different environments. Additional it will be presented a spectrometer for the ambient pressure photoemission spectroscopy with a new monochromatic source, in order to permit complete characterization of the energy, angular, and later resolutions using different metal samples at different pressures.

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5:40pm **AS+SS-ThA11 Fabrication and Characterization of Heusler-Based Fe-Mn-Ge Epitaxial Films**, *B.D. Clark*, *N. Naghibolashrafi*, *S. Gupta*, *J. Jones*, *P.R. LeClair*, *A. Gupta*, ***Gary Mankey***, University of Alabama

Half metallic alloys have a wide range of applications such as spin filters, spin polarizers, and high signal giant magnetoresistive devices. The Heusler family of alloys is predicted to have a large number of half-metallic alloys. The MINT Center at UA maintains an extensive database of Heusler alloys (http://heusleralloys.mint.ua.edu/) to track and contribute to the application of Heuslers in technology applications. The formation of stable crystal structures that match theoretical predictions is one issue that we are addressing experimentally. In this work, high temperature magnetron sputtering is applied in an attempt to stabilize predicted phases. The sputtering system is confocal with four targets, so alloy composition can be controlled by carefully adjusting the power to separate magnetron guns containing elemental targets of Fe, Mn, and Ge. Both in-situ and ex-situ techniques are applied to evaluate the resulting films. For in-situ flux monitoring, a quartz crystal microbalance is used; for in-situ chemical analysis, Auger electron spectroscopy with a cylindrical mirror analyzer is performed; and for in-situ structural analysis, reflection high-energy electron diffraction is performed. The ex-situ techniques employed include x-ray reflectivity and diffraction, scanning transmission microscopy with selected area diffraction, energy dispersive x-ray analysis, and variable temperature magnetometry and transport. Our characterization results show that when deposited on sapphire, the full-Heusler $Fe_2MnGe$ forms in the hexagonal $DO_{19}$ crystal structure instead of the predicted $L2_1$ phase. The equiatomic half-Heusler alloy of FeMnGe forms in the $C1_b$ crystal structure when deposited on MgO(100). The results underline the importance of complete complimentary characterization techniques that include both chemical and structural analysis since the principle x-ray diffraction peaks of the $L2_1$ and $C1_b$ structures occur at the same locations. The two types of alloy films that were fabricated also exhibit markedly different magnetic behavior which will be discussed in detail.

We acknowledge MINT support through shared facilities. The work was supported by NSF DMREF Grant No. 1235396.

## Biomaterial Interfaces Division
## Room: 12 - Session BI+AS-ThA

## Biomolecules and Biophysics at Interfaces
**Moderators:** Stephanie Allen, The University of Nottingham, UK, Markus Valtiner, TU Bergakademie Freiberg

2:20pm **BI+AS-ThA1 Engineering and Imaging Excitons for Brain Imaging of Modulatory Neurotransmitters**, *M. Landry*, ***Abraham Beyene***, University of California at Berkeley **INVITED**

For over 60 years, drugs that alter, mimic, or block modulatory neurotransmitters have formed the core arsenal for the treatment of neurological disorders such as depression, addiction, schizophrenia, anxiety, and Parkinson's disease. However, methods to diagnose and validate drug efficacy have remained largely the same: questionnaires and behavioral observations. The archaic nature of neurological disorder diagnosis results from the lack of tools to detect the molecular 'key players' of neuronal communication – the three primary modulatory neurotransmitters dopamine, serotonin, and norepinephrine. In this talk, we describe the design, characterization, and implementation of near-infrared optical sensors to image neurotransmitter dopamine. We show direct visualization of endogenous dopamine release over multiple rounds of acute brain slice stimulation, for over 80 minutes. We next introduce a new form of fluorescence microscopy for deep-brain neurotransmitter imaging: double infrared excitation-emission imaging. We characterize our findings in the context of their utility for high spatial and temporal neurotransmitter imaging in the brain, describe nanosensor exciton behavior from a molecular dynamics (MD) perspective, validate nanosensor use in vitro, and for nanosensor use in vivo, to correlate external stimuli (experiences, behavior) to chemical output (neurotransmission).

3:00pm **BI+AS-ThA3 Neurotrophin-like Peptides at the Interface with Gold Nanoparticles As New Nanoplatform for CNS Disorders**, ***Cristina Satriano***, *P. Di Pietro, N. Caporarello, C.D. Anfuso, G. Lupo*, University of Catania, Italy, *A. Magrì*, National Council of Research (IBB-CNR), Italy, *D. La Mendola*, University of Pisa, Italy, *E. Rizzarelli*, University of Catania, Italy

Neurotrophins are vital proteins for neural developing and maintenance as well as promising drugs in several neurodegenerative disorders.

In the present work we propose a combined approach of peptidomimetic and nanomedicine to tackle their current limits in an effective clinical application. Specifically, neurotrophin-mimicking peptides may allow for reducing some adverse side effects shown by the whole protein [1]. Moreover, the immobilisation of these peptides on nanoparticles offers many advantages, such as the protection against degradation, an enhanced permeability of barrier membranes and, if any, intrinsic nanomaterial therapeutic properties (for example, the anti-angiogenic and plasmonic features of gold nanoparticles, AuNPs) [2].

The functionalisation of spherical AuNPs of 12 nm of diameter by peptides owing respectively to the N-terminal domains of nerve growth factor, NGF1-14, and brain derived neurotrophic factor, BDNF1-12, were scrutinised both in the direct physisorption and in the lipid bilayer-mediated adsorption processes. UV-visible and X-ray photoelectron spectroscopies, QCM-D, dynamic light scattering, zeta potential analyses and atomic force microscopy were used to investigate the hybrid nano-biointerface. Both peptide- and lipid-dependant features were identified, in order to have a modulation in the nanoparticles peptide coverage as well as in the cellular uptake of NGF and BDNF peptides, as investigated by confocal microscopy. The promising potentialities in the capability to cross the blood brain barrier (BBB) were demonstrated with Human Brain Microvascular Endothelial Cells, a cell model representative of human brain endothelium that exhibits barrier properties comparable to other BBB models.

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4:00pm **BI+AS-ThA6 Controlling and Probing the Orientation of Immobilized Protein G B1 on Gold Nanoparticles Using Time of Flight Secondary Ion Mass Spectrometry and X-ray Photoelectron Spectroscopy**, ***Yung-Chen Wang***, *D.G. Castner*, University of Washington, Seattle

Nanoparticles (NPs) have been widely used in many fields of science due to their unique physical properties. While many applications of NPs such as imaging probes or drug carriers often require the conjugation of proteins or biomolecules, the surface interactions between NPs and biomolecules remains underexplored. For example, the immobilization of immunoglobulin G (IgG) onto nanoparticle surfaces is critical for the development of many immunosensors and drug delivery nanocarriers. Notably, the orientation of the immobilized IgG can have significant impact on the clinical outcomes of these carriers by impacting its biostability and efficacy.

In this work, Protein G B1, a protein that can selectively bind to the Fc tail of IgG, was immobilized onto gold NPs (AuNPs) functionalized with maleimide and oligo-(ethylene glycol)(OEG) self-assembled monolayers (SAMs). Protein G B1 was immobilized onto AuNPs through specific maleimide-cysteine interaction. As the wild type Protein G B1 does not contain a cysteine, we can strategically introduce cysteine mutants on Protein G B1 to control the location of the maleimide-cysteine bonding. We used the surface sensitive analysis techniques of x-ray photoelectron spectroscopy (XPS) and time of flight-secondary ion mass spectrometry (ToF-SIMS) to characterize the surface elemental composition, coverage, and orientation of the protein G B1 immobilization process.

XPS analysis confirmed the AuNP functionalization with the maleimide SAMs. After incubation with protein containing cysteine mutant, the immobilization of the protein was demonstrated by the increased nitrogen signal on the surface of the AuNP. Wild type Protein G B1 cannot form the maleimid-cysteine bond and was effectively removed through conventional centrifugation-resuspension washes and dialysis cleaning.

ToF-SIMS analysis also confirmed the successful functionalization and protein immobilization on the AuNPs by identifying signature secondary ions of the maleimide functional group and amino acids. Utilizing the small sampling depth (~2nm) of ToF-SIMS relative to the size of Protein G B1 (~3nm), the orientation of immobilized protein G B1 was determined by comparing the ratio of secondary ion intensity originating from the opposite regions of the protein. Overall, site-specific maleimide-cysteine interaction and systematic surface characterizations enabled us to both control and probe the orientation of immobilized proteins on AuNPs. The systematic characterization of this study provided detailed information about protein-NP interactions and a platform for controlled immobilization for IgGs on NPs.

4:20pm **BI+AS-ThA7 Angiogenin Peptides and Gold Nanoparticles for Modulated Angiogenesis Processes**, *L.M. Cucci, C. Satriano, E. Rizzarelli*, University of Catania, Italy, ***Diego La Mendola***, University of Pisa, Italy

Angiogenin (Ang) is a physiological constituent of the human plasma and is a protein overexpressed in different types of tumours [1]. Gold nanoparticles (AuNPs) exhibit anti-angiogenic activity [2] and inhibit growth factor-mediated signalling *in vitro* as well as vascular endothelial growth factor (VEGF)-induced angiogenesis *in vivo* [3].

Herein, the fragment Ang60-68, including the putative cellular binding site of the protein Ang, has been synthesized and used to functionalize spherical AuNPs of 12 nm of diameter. The Ang mimicking activity of the peptide was evaluated by the staining of actin, a key target of the entire Ang, in terms of cell cytoskeleton reorganisation.

The hybrid peptide-nanoparticle assembly was obtained by physical adsorption of the peptides at the surface of AuNPs and was analysed by UV-visible spectroscopy, in order to characterise, with titration experiments, the variations of the plasmonic properties of AuNPs as well as the peptide spectral features. Another hybrid nanosystem was prepared by the immobilisation on AuNPs of the fluorescent analogous, Fam-Ang59-68, synthetized through an amidic bond which involved the N-terminal residue with the carboxyfluorescein (Fam) moiety.

The hydrodynamic size of the peptide-Au nanosystems was determined by dynamic light scattering (DLS) analysis.

Proof-of-work experiments with human neuroblastoma cells line were carried out to prove the non-toxicity of Ang-mimicking peptide functionalised gold nanoparticles. Furthermore, laser scanning confocal microscopy (LSM) images showed the localization of the peptide-nanoparticles at the cell membrane and their sub-cellular distribution. These data reveal an auspicious new platform for imaging and therapeutic activities in angiogenesis-involved diseases.

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5:00pm **BI+AS-ThA9 Exploiting Protein-Polyelectrolyte Interactions to Control and Tune Protein Immobilization at Interfaces. Applications in Biocatalysis and Separation Technology**, *C. Dupont-Gillain, A. Bratek-Skicki, **Aurélien vander Straeten***, UC Louvain, Belgium

INTRODUCTION: For many applications in biomedical science and biotechnology, it is challenging to control and tune the nature, amount, and activity of proteins at interfaces. Since proteins are polyampholytes, they do interact with polyelectrolytes (PE), in a way which strongly depends on the pH and ionic strength of the medium. It is usually considered that PE provide a mild environment to proteins, which may help keeping their activity unaffected by surface immobilization. Here, we explore two different approaches to take advantage of the PE-protein interactions for the controlled and tunable surface immobilization of proteins.

STRATEGY: In a first approach, mixed brushes of poly(ethylene oxide) (PEO), a protein-repellent polymer, and of a negatively- or positively-charged PE, respectively poly(acrylic acid) (PAA) and poly(2-(dimethylamine)ethylmethacrylate) (PDMAEMA), were prepared by the “grafting to” approach. These stimuli-responsive mixed brushes were used to selectively adsorb/desorb a given protein from a mixture of several proteins. In a second approach, PE-protein complexes were prepared then immobilized at interfaces within layer-by-layer (LbL) assemblies. This was in particular performed for PE-enzyme complexes, including PE-lysozyme and PE-glucose oxidase complexes. Systems including several enzymes were designed, with a view to further enable enzymatic cascades. Polymer brush formation and protein immobilization were monitored using quartz crystal microbalance, X-ray photoelectron spectroscopy and time-of-flight secondary ions mass spectrometry. Gel electrophoresis was used to determine the nature of proteins collected from the interface. PE-protein complex formation was assessed based on turbidimetry and dynamic light scattering measurements. Enzyme activity was measured based on standard assays.

RESULTS: (i) *Mixed polymer brushes-protein interactions*: From adsorption experiments with single and mixed solutions of albumin, lysozyme and fibrinogen on PAA/PEO and PDMAEMA/PEO brushes, it was demonstrated that the selective adsorption of one protein could be achieved, as well as the sequential desorption of these proteins when the three of them were adsorbed initially, by means of appropriate pH and I triggers. (ii) *PE-enzyme complexes as building blocks for LbL assembly*: PE-enzyme complexes were successfully built and characterized, then incorporated into LbL assemblies. The specific activity of lysozyme was higher when immobilized as a complex rather than in its native form.

CONCLUSION:The developed systems may find direct applications in separation technology, on the one hand, and in biocatalysis, on the other hand.

5:20pm **BI+AS-ThA10 Determination of Confined Molecular Structure by using X-ray-Surface Force Apparatus (XSFA) Study in Bio-interface Application**, ***Hsiu-Wei Cheng**, M. Valtiner,* Technical University Freiberg, Germany*, C. Merola,* Max-Planck Institute for Iron Research, Germany*, K. Schwenzfeier,* Technical University Freiberg, Germany*, M. Mezger, H. Weiss*, Max-Planck Institute for Polymer Research, Germany

In biology system, understanding of molecular dynamics at confined interface such as medicine diffusion across inter-cellular channel, lubrication at joints and electric signal transmission from nerves to nerves is boosting the modern medical and biomaterial study. To study the behavior of confined molecules in detail, a home-build X-ray surface force apparatus (XSFA) which combines a synchrotron X-ray with white light interferometry is used. In our first step, an imidazolium chloride based ionic liquid, which consists of a clear water induced phase change, was used as a modeling system to test the detection limit of XSFA. The result shows that the liquid phase change from liquid to liquid crystal can be clearly distinguished within a 50 to 100 nm confinement. Meanwhile, the application of X-ray reflectivity (XRR) reveal furthermore in-plane ordering information of the liquid crystal structure. Secondly, shear force were applied to study how confined liquids react to the friction to mimic the motion of joint. We found that friction behavior and molecular dynamics are strongly related to the gap size of the confinement, which is a useful information for artificial joint design. The combination of SFA and synchrotron X-ray has shown a great analytical potential to solve the interfacial molecular dynamic, which provides scientists another powerful tool to peer the world of molecule.

6:00pm **BI+AS-ThA12 Direct Quantification of the Hydrophobic-to-Hydrophilic Transition of Interaction Forces**, ***Laila Moreno Ostertag**, T. Utzig, P. Stock,* Max Planck Institute for Iron Research, Germany, *M. Valtiner*, TU Bergakademie Freiberg, Germany

When two surfaces come in close contact, several forces arise and, depending on the nature of the surfaces, these forces will show different magnitude. This principle may also be applied to diverse biological systems. Van der Waals forces have been on the radar for a century or so, and the identification of electrostatic interactions can be traced back to ancient times. It has also been clear that the behavior of such surfaces in terms of their polarity is associated to another type of force, called hydrophobic interactions.[1,2] The combination of these contributions leads to a better understanding of the interactions as the surfaces get closer together.

In this regard, we have revisited the hydrophobic interactions theory by studying the interaction forces between apposing symmetric surfaces of varying hydrophobicity via Atomic Force Microscopy and correlating them to the behavior of water at the interface. Short hydrophobic chains ending in either non-polar, hydrophobic groups or in charged heads and combinations of them were attached to smooth surfaces and tested under constant ionic force conditions. Mathematical modeling of the interactions was applied to the experimental results in order to obtain numerical parameters that are associated to the surface properties. Interesting results that are in apparent contradiction with the expected trend of the hydration parameters were found but can be explained by what we suggest is a breakdown of the water structure at the interface, which in turn can contribute to the understanding of attraction or repulsion between certain biological systems in aqueous media.

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## Electronic Materials and Photonics Division
## Room: 14 - Session EM+NS-ThA

## Wide and Ultra-wide Band Gap Materials for Electronic Devices: Growth, Modeling, and Properties

**Moderators:** Michael Filler, Georgia Institute of Technology, Rachael Myers-Ward, U.S. Naval Research Laboratory

2:20pm **EM+NS-ThA1 Synthesis of β-Ga2O3 Thin Films on SiC by Molecular Beam Epitaxy**, ***Neeraj Nepal**, D.S. Katzer, D.F. Storm, M.T. Hardy, B.P. Downey, D.J. Meyer*, U.S. Naval Research Laboratory

Recently, there has been great interest in β-Ga2O3 as a next generation ultra-wide bandgap semiconductor (UWBGS) for high-power/temperature electronics devices. However, it has low thermal conductivity of β-Ga2O3 may limit device performance. One strategy to improve performance of Ga2O3 based devices is through heterostructure design on high thermal conductivity substrate. In this paper, we report growth and characterization of 100 nm thick β-Ga2O3 on SiC by molecular beam epitaxy (MBE) at 650 °C. First, the growth parameter space such thermocouple measured growth temperature, relative Ga flux, and oxygen plasma were varied to grow β-Ga2O3 films on c-plane sapphire substrates. For an O2 plasma flow of 1 sccm (2.5x10-5 torr) X-ray diffraction shows weak facets of β-Ga2O3 appear regardless of the Ga flux and temperature, however for <0.6 sccm O2 flow, smooth β-Ga2O3 [ (-201)||(0001)] grows on c-plane sapphire. Optimized MBE growth conditions on sapphire substrate were used to grow β-Ga2O3 on SiC. Single phase MBE β-Ga2O3 film on SiC grown at 650 °C are insulating, have rocking curve full-width-at-half-maximum of 720 arc-sec with root mean square surface roughness of less than 2 nm. In this paper we will discuss MBE growth parameter space of β-Ga2O3 on sapphire and the structural, morphological, and electrical properties of MBE grown β-Ga2O3 thin films on SiC.

2:40pm **EM+NS-ThA2 Growth and Characterization of *α*-, *β*-, and *ε*-$Ga_2O_3$ Epitaxial Layers**, ***Lisa Porter**, Y. Yao, L.A.M. Lyle,* Carnegie Mellon University*, S. Okur, G.S. Tompa, T. Salagaj, N. Sbrockey*, Structured Materials Industries, Inc.

Increasing global demand for energy makes urgent the need for highly efficient high-power electronics for energy conversion and transport. Although silicon devices have been traditionally used for high-power electronics, wide bandgap semiconductors (e.g., SiC and GaN) are much more efficient for these applications, because they can withstand higher electric fields with less material and reduced energy loss. However, the substrates of both materials are still very expensive. A very promising alternative to SiC and GaN is gallium oxide, $Ga_2O_3$, which has an even larger bandgap than the former two materials. The availability of this material presents new possibilities for disruptive devices and technologies that could translate to even greater energy efficiencies at lower cost than predicted for SiC and GaN. Polished 2-in diameter, single-crystal wafers of the monoclinic $\beta$-phase can be grown using melt-growth methods and are commercially available. However, there is increasing interest in the other $Ga_2O_3$ phases, particularly the metastable corundum-structured $\alpha$- and hexagonal-structured $\varepsilon$-$Ga_2O_3$ phases because of their higher symmetry and simpler epitaxial relations to c-plane sapphire, in addition to the possibility of producing functional heterostructures or tunable bandgaps through alloying. We have successfully grown epitaxial films of $\alpha$-, $\beta$- and $\varepsilon$-phases on c-plane sapphire using different precursors and growth conditions. The $\alpha$- and $\varepsilon$-phases have generally been reported in the literature to form at lower growth temperatures than the $\beta$-phase. However, we observed a change in phase formation at the same growth temperature by changing our growth technique and Ga precursor from metalorganic chemical vapor deposition (MOCVD) and trimethlygallium to halide vapor phase epitaxy (HVPE) and gallium chloride. Data from x-ray diffraction, scanning electron microscopy and high-resolution transmission electron microscopy will be presented to illustrate the different epitaxial films and orientation relationships. The results of secondary ion mass spectrometry depth profiles, which showed compositional differences within the different phases, will also be presented. The authors wish to acknowledge the Office of Naval Research under contract no. N00014-16-P2059.

3:00pm **EM+NS-ThA3 Ultra-wide-bandgap $Ga_2O_3$ Material and Electronic Device Technologies**, ***Masataka Higashiwaki***, *M.H. Wong,* National Institute of Information and Communications Technology, Japan, *K. Konishi,* Tokyo University of Agriculture and Technology, Japan, *Y. Nakata, T. Kamimura,* National Institute of Information and Communications Technology, Japan, *K. Sasaki, K. Goto,* Tamura Corporation, Japan, *A. Takeyama, T. Makino, T. Ohshima,* National Institutes for Quantum and Radiological Science and Technology, Japan, *H. Murakami, Y. Kumagai,* Tokyo University of Agriculture and Technology, Japan, *A. Kuramata, S. Yamakoshi,* Tamura Corporation, Japan **INVITED**

Recently, gallium oxide ($Ga_2O_3$) has attracted much attention as a candidate for future power and harsh environment electronics due to its extremely large bandgap of 4.5 eV and the availability of economical melt-grown native substrates. In this talk, following a short introduction of the material properties of $Ga_2O_3$, we will discuss our recent progress in the development of $Ga_2O_3$ metal-oxide-semiconductor field-effect transistors (MOSFETs) and Schottky barrier diodes (SBDs), including $Ga_2O_3$ thin-film epitaxial growth technologies by molecular beam epitaxy (MBE) and halide vapor phase epitaxy (HVPE).

State-of-the-art $Ga_2O_3$ MOSFETs with a gate-connected field plate (FP) were fabricated using MBE-grown $Ga_2O_3$ homoepitaxial layers. The devices showed excellent room-temperature (RT) characteristics such as a record high off-state breakdown voltage ($V_{br}$) of 755 V, a large drain current on/off ratio of over nine orders of magnitude, and DC-RF dispersion-free output characteristics [1]. Furthermore, the MOSFETs demonstrated strong prospects of $Ga_2O_3$ devices for extreme environment electronics by virtue of their stable high-temperature operation up to 300°C and strong radiation hardness against gamma-ray irradiation [2].

We have also fabricated and characterized $Ga_2O_3$ FP-SBDs on $n^-$-$Ga_2O_3$ drift layers grown by HVPE [3-5]. The illustrative device with a net donor concentration of $1.8\times10^{16}$ $cm^{-3}$ exhibited a specific on-resistance of 5.1 $m\Omega\cdot cm^2$ and an ideality factor of 1.05 at RT. Successful FP engineering resulted in a high $V_{br}$ of 1076 V. Note that this was the first demonstration of $V_{br}$ of over 1 kV in any $Ga_2O_3$ power device. The maximum electric field in the $Ga_2O_3$ drift layer at the condition of destructive breakdown was estimated to be 5.1 MV/cm by device simulation, which is about two times larger than the theoretical limits for SiC and GaN.

This work was partially supported by Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), "Next-generation power electronics" (funding agency: NEDO).

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4:00pm **EM+NS-ThA6 Reactive Magnetron Sputtering of Titanium Nitride and Titanium Aluminum Nitride on Lithium Niobate for Electronic and Opto-Electronic Applications**, ***Amber Reed***, *H.A. Smith, D.C. Abeysinghe, P.J. Shah, L. Grazulis, M.J. Hill, M.E. McConney, B.M. Howe, A.M. Urbas,* Air Force Research Laboratory

High temperature stability, hardness, abrasion resistance, chemical stability and potential complimentary metal-oxide semiconductor process compatibility, combined with a high electrical conductivity make titanium nitride (TiN) an important material for electronic and opto-electronic applications. TiN is particularly important as an electrode material due to its oxidation resistance, which can be improved by alloying it with aluminum nitride to form titanium aluminum nitride ($Ti_{1-x}Al_xN$). In addition to its use as an electrode, TiN is also a promising plasmonic material because, similar gold, it possesses a zero crossover wavelength in the visible region. The ability to synthesize high quality TiN crystals on different electronic substrates would greatly facilitate its incorporation in electronic and opto-electronic devices. One particular material of interest is lithium niobate ($LiNbO_3$), which possesses unique piezoelectric, opto-electronic and nonlinear optical properties. Synthesis of high quality TiN on $LiNbO_3$ would allow for integration of TiN into acoustic devices (i.e. SAWs and BAWs), optical modulators, and other electronic and opto-electronic devices.

In this work, we demonstrate the synthesis of high quality epitaxial TiN crystals on Z-cut $LiNbO_3$ substrates. We also discuss the growth of TiN and $Ti_{1-x}Al_xN$ on Y-cut $LiNbO_3$. While the (001) plane of Z-cut $LiNbO_3$ creates a template for epitaxial growth of (111)-oriented TiN crystals, similar to growth on (001)-oriented sapphire, the (010) plane of Y-cut $LiNbO_3$ is equally lattice matched to the TiN (001) and (101) planes which results in competitive growth of those two orientations. Alloying the TiN with AlN exacerbates this issue as the lattice constant shrinks with increased AlN content. We investigate the role of deposition power, nitrogen gas fraction, and substrate temperature and ion flux impingement on the competitive growth to determine the optimal growth conditions to promote epitaxy. Films are characterized using x-ray diffraction (XRD), atomic force microscopy (AFM), transmission electron microscopy, ellipsometry and electrical measurements. XRD and AFM of TiN on Z-cut $LiNbO_3$ show remarkably smooth (< 220 pm RMS roughness) epitaxial films. Ellipsometry measurements of the TiN on Z-cut $LiNbO_3$ reveal carrier concentrations up to 4.0 $x10^{22}$ $cm^{-3}$, mobilities of ~3.2 $cm^2/(V\ s)$ and a $\varepsilon_1/\ \varepsilon_2$ of 1.00 to 3.34 at a wavelength of 1550 nm.

4:20pm **EM+NS-ThA7 Growth and Property Analysis of Doped GaN-GaAlN Heterostructures on Low- and High-temperature AlN/Sapphire Templates**, ***Nikolaus Dietz***, *B.G. Cross, M. Vernon,* Georgia State University, *R. Collazo, R. Kirste, S. Mita, Z. Sitar,* North Carolina State University

The developing of radiation-hard UV solid state avalanche photodiodes (APD's) based on group III-Nitride wide band gap materials have a wide application area from solar blind detector to wavelength specific PMT based detector devices that can be tuned in the 220 nm to 450 nm wavelength range, tailored to specific scintillators of interest. This contribution focuses on closely lattice-matched, high-quality GaN a substrate technologies using metalorganic chemical vapor deposition (MOCVD) technique, which provide sufficient high-quality AlGaN layers and heterostructures with high phase uniformity and low dislocation density for low leakage currents, to enable avalanche mechanisms, low leakage currents, high performance characteristics and reliability of the devices.

We will present results on the growth and doping of GaN/GaAlN heterostructures deposited on low- and high-temperature AlN/Sapphire template structures, using a customized D125 Veeco MOCVD reactor system. The structural quality of the initial GaN layer grown on various AlN-/GaN-sapphire template structure has been analyzed and is accessed regarding its resulting dislocation and defect densities, using XRD, Raman and FTIR spectroscopy. The influence of Silicon n-doping in GaN and $Ga_{0.9}Al_{0.1}N$ epilayers on the defect density was analyzed XRD and the dopant incorporation by SIMS analysis.

4:40pm **EM+NS-ThA8 A Thermodynamic Supersaturation model for the Growth of AlGaN by MOCVD**, ***Ramón Collazo***, *S. Washiyama, I. Bryan,* North Carolina State University, *P. Reddy, S. Mita,* Adroit Materials Inc., *Z. Sitar,* North Carolina State University **INVITED**

AlGaN have been considered to be essential for the development of optoelectronic and electronic devices such as deep UV LEDs and other power devices. However, even under well-controlled growth conditions it is difficult to precisely predict the behavior of AlGaN growth with regards to Al-concentration and related defect incorporation. We have developed a thermodynamic model for the calculation of the Ga supersaturation during the growth of GaN by metalorganic chemical vapor deposition (MOCVD), which was successfully used to predict incorporation of impurities such as carbon as well as the surface morphology (Mita et al., JAP 104, 13521). This model was extended to evaluate the supersaturation of Al and Ga in AlGaN growth and to allow for the prediction of the properties of MOCVD grown AlGaN layers. Non-linear equations for Al and Ga equilibrium vapor pressure calculation describe the process under the following assumptions: (1) under low total pressure, gas phase reactions between the metalorganics and $NH_3$ are negligible; the III metal precursors are irreversibly cracked on the growth surface, thus, Al, Ga, $NH_3$, $H_2$ and $N_2$ are analyzed; (2) number of moles of growing species are conserved; (3) at least some $NH_3$ molecules are thermally cracked in the gas phase. Using the resulting model, the influence of growth parameters such as V/III and flow rate on AlGaN growth was determined through the dependence of the Ga and Al supersaturation. The independent parameters for the calculations included the growth conditions that were set by typical conditions for AlGaN MOCVD growth. Calculation showed a significantly lower equilibrium vapor pressure for Al ($10^{-12}$-$10^{-16}$ Torr) than for Ga ($10^{-4}$-$10^{-6}$ Torr). The Ga equilibrium pressure monotonously decreased with increasing V/III ratio, while $NH_3$ thermal cracking was more significant on the equilibrium pressure, as expected from Le Chatelier`s principle. The significant difference in the supersaturation between Ga and Al has a significant influence on the growth of ternary AlGaN compounds and need to be considered for finding appropriate and robust growth conditions at high temperatures, exceeding 1150 ºC. A processing AlGaN compositional phase diagram dependent on the typical growth conditions will be presented. In addition, experimental validation of this model with respect to Al composition, process stability and robustness will be discussed. This validation will be presented in terms of temperature and V/III ratio.

5:20pm **EM+NS-ThA10 Anomalous Hall Effect in MOCVD-grown Gadolinium-doped Gallium Nitride**, *V.G. Saravade, P. Patel, C. Ferguson, K. Yunghans, A. Ghods, C. Zhou,* ***Ian Ferguson***, Missouri University of Science and Technology

Dilute Magnetic Semiconductor (DMS) materials for spintronics applications have the potential to reduce power consumption while increasing the processing speed, integration densities and non-volatile memory, compared to the conventional semiconductor devices. While Gd-doped GaN has exhibited room temperature (RT) ferromagnetism, the Anomalous Hall Effect (AHE) has not been reported in relation to the observed magnetic properties [1, 2].

In this work, we study the AHE in MOCVD-grown Gd-doped GaN with different Gd concentrations and precursors, and investigate their magnetic properties. RT AHE along with XRD helps in determining the mechanisms responsible for the observed ferromagnetism. Our preliminary measurements showed residual $R_{xy}/R_{xx}$ up to 10 and residual coercive field up to 50 Oe. These hysteresis curves can be caused by the ferromagnetic properties of MOCVD-grown Gd-doped GaN. Additionally, GaN (002) peak had been identified in the initial Ω-2θ XRD scans. XRD rocking curve scans with varying Ω will be performed to study, the defects that are induced by doping GaN with Gd, and their potential contribution towards ferromagnetism. AHE and XRD results of Gd-doped GaN will be compared to those of un-doped GaN to verify that the ferromagnetism is caused by Gd doping. Furthermore, the effect of temperature on the magnetic behavior of Gd-doped GaN will be analyzed using variable temperature AHE.

To our knowledge, we are the first to report the AHE in MOCVD-grown Gd-doped GaN. We consider this work to contribute towards the investigation of DMS for RT ferromagnetism and further for spintronics applications.

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5:40pm **EM+NS-ThA11 Valence and Conduction Band Offsets of $Al_2O_3$, $LaAl_2O_3$, AZO and ITO with $Ga_2O_3$**, ***Patrick Carey IV****, F. Ren, D. Hays, B. Gila, S.J. Pearton,* University of Florida, *S. Jang,* Dankook University, South Korea, *A. Kuramata*, Tamura Corporation, Japan

Band alignments for $Al_2O_3$, $LaAl_2O_3$ (LAO), Aluminum Zinc Oxide (AZO), and Indium Tin Oxide (ITO) with bulk β-$Ga_2O_3$ were determined by X-ray Photoelectron Spectroscopy. β-$Ga_2O_3$ is a direct band gap, ~4.9 eV, semiconductor, it has a very high theoretical breakdown electric field (~8 MV/cm), and is suitable for high power electronics in industrial, military applications, deep-UV photodetectors for a cut-off wavelength of 280 nm, and high temperature gas sensors. Ohmic contact with low contact resistance and gate oxides with low leakage current are essential for fabricating high performance base $Ga_2O_3$ electronic and optical devices. Since $Ga_2O_3$ has a wide energy bandgap, it is difficult to form low resistance Ohmic contact with conventional metal contact. ITO and AZO were found to have a conduction band offset of gap of -0.32 and -0.79 eV, respectively, which can be used as an intermediate layers between the metal contact and $Ga_2O_3$ to reduce contact resistance on $Ga_2O_3$-based devices. For wider energy band oxides, for use as gate oxides, sputtered LAO, atomic layer deposited (ALD) and rf-magnetron sputtered $Al_2O_3$ were employed. LAO was found to have a bandgap of 6.5 eV, a valence band offset of -0.21 eV, and a conduction band offset of 2.01 eV. LAO has a type II alignment and would provide excellent electron confinement, but no barrier for hole transport. $Al_2O_3$ was found to have a bandgap of 6.9 eV regardless of preparation method. However, the deposition method affected the band alignment. For ALD $Al_2O_3$, it has a has a nested (type I) gap alignment with a valence band offset of 0.07eV and a conduction band offset of 2.23 eV. While for sputtered $Al_2O_3$ on the same $Ga_2O_3$, there is a type II alignment with a valence band offset of -0.86 eV and a conduction band offset of 3.16 eV. The conduction band offsets in either case are large and provide excellent electron confinement, but the valence band offsets are smaller than desirable for limiting hole transport.

6:00pm **EM+NS-ThA12 *In Situ* Plasma Emission Spectroscopy of InN/GaN Heterostructures Grown by MEPA-MOCVD**, ***Daniel Seidlitz****, B.G. Cross, Y. Abate*, Georgia State University, *A. Hoffmann,* Technical University of Berlin, Germany, *N. Dietz*, Georgia State University

In this study, we will present results of the in-situ plasma emission spectroscopy (PES) of the plasma activated nitrogen species during the growth of GaN/InN heterostructures by MEPA-MOCVD in correlation to their optical and structural characteristics.

Indium-rich InGaN semiconductors are of high interest due to the high electron mobility which enables ultrafast electronics operating in the THz regime. In conventional MOCVD, indium incorporation above 25 % is a challenge due to the vastly different partial pressures between InN and GaN and the lattice mismatch between the binaries. Migration enhanced plasma-assisted MOCVD is a kinetic stabilized growth surface approach to reduce the partial pressure difference between the InN and GaN. It also replaces the traditional ammonia precursor source for nitrogen through energetically controlled ionized nitrogen species (N*/NH*/NHx*), generated by a radio-frequency hollow cathode (13.56 MHz) with an output power between 50-600 W. The plasma-excited species are tailored in the gas phase and directed to the growth surface in the afterglow regime of the remote plasma utilizing the kinetic energies of the active nitrogen species to achieve a stable growth surface. Altering the process parameters like reactor pressure and nitrogen flux allows variation of the kinetic energies. A grid between the plasma source and the growth surface enables the control of the charged species reaching the growth surface and with it the electrostatic interactions in the InN/GaN growth process and the resulting layer properties. In-situ real-time plasma emission spectroscopy (PES) is used to monitor and identify the active nitrogen species close to the hollow cathode as well as near the growth surface. Comparison of the spectra could help to determine which nitrogen species promote the growth of group III- nitride materials.

Optoelectronic and structural qualities such as free carrier concentration as well as crystallinity, growth rate, the surface morphology of the GaN and InGaN films are examined using ex-situ characterization techniques (Raman, AFM, FTIR). We will present a correlation of the in-situ and ex-situ results as a function of the explored growth parameters like growth temperature, plasma power, and reactor pressure.

## Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
## Room: 24 - Session HC+SS-ThA

## Combined Experimental and Theoretical Explorations of the Dynamics of Heterogeneously Catalyzed Reactions
**Moderator:** L. Gabriela Avila-Bront, College of the Holy Cross

2:20pm **HC+SS-ThA1 Building the World's Greatest Microscope: Revealing the Atomic Scale Dynamics of Surface Chemistry**, *A. Wodtke,* Max Planck Institute for Biophysical Chemistry, Germany, *O. Buenermann, H. Jiang, Y. Dorenkamp,* Institute for Physical Chemistry University of Goettingen, Germany, *A. Kandratsenka, S.M. Janke,* ***Daniel Auerbach***, Max Planck Institute for Biophysical Chemistry, Germany **INVITED**

In 1929, Nobel Laureate Paul Dirac made comments to the effect that Chemistry had been solved. With the advent of quantum mechanics "The underlying physical laws necessary for the mathematical theory of… …the whole of chemistry are… …completely known…. However, on a practical level computational chemistry is still in an early stage of development. Dirac went on: "the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." Despite electrifying advances in computational power since that time, Dirac is still right. The theory of chemistry requires approximations before theoretical descriptions and predictions of chemical reactions can be made.

The advent of the Born-Oppenheimer Approximation led to the development of the standard model of chemical reactivity where the electronically adiabatic potential energy surface for nuclear motion is derived and quantum motion of the nuclei on that surface can be calculated. For simple gas phase reactions, this approach has become an extraordinarily useful and reliable tool. For surface chemistry, additional approximations are commonly made: 1) classical mechanics for describing nuclear motion, 2) density functional theory (usually at the generalized gradient level) for calculating electronic states, 3) reduced dimensionality approximations and as before 4) the Born-Oppenheimer approximation to separate electronic and nuclear degrees of freedom. I call this collection of approximations the provisional model for surface chemistry as we in the field are still testing and improving it.

In this talk, I will describe how a fruitful interplay between experiment and theory can lead to accurate atomic-scale simulations of simple reactions at metal surfaces. I will describe the very significant challenges surface chemistry presents including the problems of high dimensionality and the common failure of the Born Oppenheimer approximation. I will present two concrete examples. In the first, results of a full dimensional experimentally validated theoretical approach to hydrogen atom adsorption at a metal surface that includes the effects of Born-Oppenheimer failure leads to an atomic scale view of H-atom adsorption at a noble metal as well as an explanation for chemicurrents. In the second, energy loss dynamics occurring on a 25-fs time scale can be inferred from the scattering of hydrogen atoms from a graphene surface where a transient C-H chemical bond is formed. The H interaction on graphene is strongly influenced by the choice of metal substrate upon which the graphene is grown.

3:00pm **HC+SS-ThA3 Calibrating Electronic Structure Calculations – A Joint Experimental-Theoretical Approach**, ***Arthur Utz***, *E.K. Dombrowski, E. High*, Tufts University

Computational chemistry holds great promise for guiding the design of new catalytic materials, but current density functional theory (DFT) methods typically do not provide the level of absolute chemical accuracy ($\Delta E \leq 1$kcal $\approx 4$ kJ/mol) required to distinguish between potential catalysts with similar activation energies, nor can they accurately predict product selectivity when the rate-limiting barriers to different reaction products are similar. Two factors are primary contributors to this shortcoming. First, the most widely used DFT functionals for reactions on metals (PBE and RPBE) are not quantitatively accurate, and are prone to systematic errors that either over- or underestimate barrier heights. Second, few experimental measurements provide accurate and unambiguous benchmarks for testing DFT predictions.

In this contribution, we will describe recent results from a joint experimental-computational study to address these limitations. We performed conventional and internal state-resolved beam-surface reactivity measurements for tri-deutero methane ($CHD_3$) molecules incident on a clean Ni(111) surface to obtain robust benchmark data for comparison with theory. Our collaborators in the Kroes group at Leiden University then used these data to "calibrate" a hybrid functional based on a linear combination of PBE and RPBE functionals via the specific reaction parameter density functional theory (SRP-DFT) approach. *Ab initio* molecular dynamics (MD) calculations using the SRP-DFT functional yielded predictions of initial reaction probability, $S_0$ as a function of incident translational energy, $E_{trans}$, for comparison with experiment.

We used measurements of $S_0$ for $CHD_3$ molecules predominantly in their vibrational ground state (v=0) and incident at the lowest incident translational energy ($E_{trans}$) studied to constrain the define the SRP-DFT functional. We then used that functional, without further modification, to predict the reactivity of a thermal ensemble of $CHD_3$ molecules whose reactivity was dominated by C-D stretching and bending vibrations, as well as of the laser excited C-H stretching states, over a wide range of $E_{trans}$. We found that despite the significant difference in energy distribution within these three ensembles of molecules, the single SRP-DFT functional yielded chemically accurate predictions of reactivity. The presentation will outline our approach and results on this system, as well as more recent work exploring the generality of this approach to other chemical systems and surface structures.

3:20pm **HC+SS-ThA4 $CO_2$, CO and $H_2O$ on Copper Surfaces: A HPXPS Study Supported by DFT Calculations**, *A. Regoutz, G. Kerherve, J.M. Kahk, J. Lischner*, ***David Payne***, Imperial College London, UK

$CO_2$ is a source for the production of carbon based fuels, including methanol, and presents an attractive alternative to fossil fuels. Copper is an ideal catalyst for the reduction of $CO_2$, as it is able to direct reactions through stable intermediates, e.g. CO. For example important questions concern the influence of oxygen on the catalytic activity and whether oxides are formed on the surface, and the role of $H_2O$ and CO (as co-adsorbents) during exposure to $CO_2$. As copper-based systems are an excellent material for the reduction of $CO_2$ a detailed understanding of the basis of its catalytic activity is essential and absolutely necessary for any further development.

X-ray photoelectron spectroscopy (XPS) is used widely in solid-state science but due to its nature as an ultra high vacuum technique (pressure $10^{-10}$ mbar) it is not possible to study more realistic gas-solid interfaces. High-pressure XPS (HPXPS) is an advanced method which allows the measurement of solid samples at elevated pressures of between 1 and 30 mbar [1]. Over the last few years, this technique has been applied to understanding the chemistry of $CO_2$ (and mixtures of gases) on copper surfaces [2-4] leading to a number of surface mechanisms being postulated.

This work presents results on the interaction of $CO_2$ with a variety of Cu surfaces (polycrystalline and single-crystals) by HPXPS. In contrast to previously published work, these experiments are supported by state-of-the-art density functional theory calculations, in an effort to enable accurate determinations of the binding energies of the various surface-bound species present during reaction.

It is hoped that the presented results provide a starting point for the detailed understanding of these copper surfaces, using HPXPS in conjunction with theory, and lead to the identification unknown phenomena.

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[3] B. Eren et al. J. Am. Chem. Soc., **138**, 8207 (2016)

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4:00pm **HC+SS-ThA6 Dissociative Adsorption of Methane on Transition Metal Surfaces and Supported Atoms from First Principles Calculations**, ***Heriberto Fabio Busnengo***, CONICET and Universidad Nacional de Rosario, Argentina **INVITED**

The study of dissociative adsorption of methane on transition-metal surfaces and transition-metal atoms deposited on oxide surfaces is of great importance to understand the reaction mechanisms governing the catalytic steam reforming process used to produce molecular hydrogen. In particular, the understanding of the origin of the role of surface temperature, surface defects involving reduced coordination metal atoms, and possible effects of the oxide support have significantly increased during the last years thanks to both, experiments and first principles calculations.

In this talk we will describe and discuss some of these recent advances by focusing on theoretical developments allowing us today, to model with unprecedented accuracy the interaction of methane with transition metal atoms under ultra high vacuum conditions and in particular, molecular beam experiments. This has been possible in part, thanks to the increase of processing power of modern computers, to methodological developments allowing to describe quantum mechanically the molecule-surface interaction dynamics, and new methods to accurately represent full dimensional interaction potentials from first principles calculations.

4:40pm **HC+SS-ThA8 Methane Steam Reforming: Using External Electric Fields to Enhance the Catalytic Performance of Ni-based Catalysts**, ***Fanglin Che***, University of Toronto, Canada, *J. Gray, S. Ha, J.-S. McEwen*, Washington State University

According to the Annual Energy Outlook, natural gas production in the U.S. is projected to continue rising through 2040. To make the most of this abundant natural resource and at the same time reduce emissions of harmful greenhouse gases it is imperative that we fully understand the catalytic reactions which are used in methane processing – particularly methane steam reforming (MSR). MSR is our reaction of interest also because the conversion of methane to syngas greatly affects the charge-transfer chemistry and consequently influences the SOFCs' performance. There are two significant issues facing MSR: (i) Coke formation; (ii) High temperatures of above 900 K. To address these issues, we are interested in the effect of an electric field on this process. [1,2]

Based on a field-dependent microkinetic model of the MSR reaction and corresponding experimental evidence, we find that a positive electric field can significantly enhance the methane conversion and reduce the formation of coke over a pure Ni surface. [3-8] The reason for such an improvement can be correlated with the fact that a positive field polarizes the Ni surface with a partial positive charge, which assists the first C-H bond cleavage of a methane molecule. [9] Changing the oxygen vacancy concentration and increasing the applied electric field value affects the charge of the Ni cluster in a Ni/YSZ cermet as well. Interestingly, we find that the C-H bond cleavage of methane becomes more favorable as the Ni cluster becomes more positively charged. We also find that the carbon complex resulting from the dissociation of a CH molecule at the triple phase boundary region of a Ni/YSZ cermet results in a more positively charged Ni cluster, which facilitates the cleavage of the first C-H bond in methane as compared to when the carbon complex is absent. This indicates that the initial carbon species resulting from the decomposition of methane assists in the first C-H bond cleavage of a methane molecule rather than the formation of coke that poisons the Ni-based catalyst. Overall, this work provides valuable information for a new design of electrochemical systems to enhance methane activation.

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5:00pm **HC+SS-ThA9 Mullite Support Boosts Active Oxygen Atoms for Enhanced Platinum Sub-nanometer Clusters Catalysis**, ***Xiao Liu***, *J.M. Cai, B. Shan, R. Chen*, Huazhong University of Science and Technology, China

Platinum (Pt) catalysts have been widely utilized in catalysis due to their excellent catalytic activity, such as CO oxidation, water-shift gas reaction and preferential CO oxidation in hydrogen. As the high cost and large demand of Pt, the improvement of its catalytic efficiency has attracted great attention to reduce its loading. Since catalytic reactions usually happen on surface, the decreasing of Pt catalyst's size to increase the fraction of exposed atoms is a widely accepted strategy to try to utilize each Pt atom. However, the low temperature activities of the Pt sub-nanometer clusters and single atoms have been greatly limited due to the seriously CO poison effect, which prevents the supplying of active oxygen. Therefore, searching new approaches to supply active oxygen atoms at low temperature is important to enhance the activity and efficiency of Pt catalysts. In this work, the density functional theory (DFT) calculations shows that the designed Pt cluster supported on $SmMn_2O_5$ mullite structure exhibits high activity for O2 dissociation than pure $SmMn_2O_5$ surface. Inspired by the theoretical results, we have prepared uniform and high dispersed sub-nanometer Pt clusters on $SmMn_2O_5$ supports ($Pt_n/SmMn_2O_5$) via atomic layer deposition method. The interfacial structure of $Pt_n/SmMn_2O_5$ characterized by high-resolution transmission electron microscopy agrees well with our designed model. The as-prepared $Pt_n/SmMn_2O_5$ catalyst has shown outstanding room temperature CO oxidation activity and low apparent activation energy, which could result from the strong interfacial interactions as indicated by the X-ray photoelectron spectra and X-ray absorption fine structure results. The *in-situ* diffuse reflectance infrared Fourier transform spectroscopy, $^{18}O$ isotope-labelling experiments and DFT calculations shows that the active oxygen supplied by the $SmMn_2O_5$ surface is critical to the room temperature CO oxidation activity.

5:20pm **HC+SS-ThA10 Calorimetric Energies of Small Adsorbates on Ni(111) and NiO(111) Surfaces, with Comparison to Pt(111) to Explain Differences in Catalytic Activity between Ni vs Pt**, ***Wei Zhao***, *S. Carey, Z. Mao, S. Morgan, C. Campbell*, University of Washington

Catalysts based on nickel and nickel oxides are of great importance in chemical industry, such as methane steam reforming and biomass conversions. We present here calorimetric measurements of the energies of several catalytically relevant adsorbed intermediates on Ni(111), including methyl, bidentate formate, $H_2O$, benzene and phenol, and also the enthalpies of $H_2O$ and HCOOH dissociative adsorption on NiO(111). We will also give an extensive comparison of these energies on Ni(111) to previous calorimetric measurements on Pt(111), providing the insight into the catalytic properties and reaction efficiency for these two metals. Besides the crucial importance of these measured energies for understanding related catalytic relations, they also provide important experimental benchmarks that can be used to improve the accuracy of the related quantum mechanical calculations.

5:40pm **HC+SS-ThA11 Defect Formation on $MoS_2$ via Methanol to Methoxy Conversion**, ***Prescott Evans***, *H.K. Jeong, S. Beniwal, P.A. Dowben*, University of Nebraska - Lincoln, *D. Le, T.S. Rahman*, University of Central Florida

Coverage dependent defect formation, via methanol adsorption on $MoS_2$ and conversion into methoxy, was investigated utilizing scanning tunneling microscopy, photoemission and modeled by density functional theory (DFT). The adsorption of methanol on $MoS_2$ at 110 K followed by annealing of the sample near 350 K or the adsorption of methanol on $MoS_2$ at 350 K results in the formation of numerous point defects at the surface of the $MoS_2$ substrate. Larger multi-point defects, nominally ~1 nm in size as well as line defects on the $MoS_2$ sample surface become increasingly apparent with multiple cycles of methanol exposure and annealing. X-ray spectroscopy studies of the exposure of $MoS_2$ to methanol are consistent with a conversion to methoxy, and the production of defects, based on the reaction kinematics, and the significant shifts in oxygen binding energies. The experimental results indicate a small but persistent activation energy for the reaction. The energy favorability of the combination of defect creation and methoxy formation is also suggested by density functional theory. A strongly bound methanol surface species is not favored on the defect free $MoS_2$ surface.

## Advanced Ion Microscopy Focus Topic
## Room: 7 & 8 - Session HI+NS+TR-ThA

## Novel Beam Induced Surface Analysis and Nano-Patterning

**Moderators:** Anne Delobbe, Orsay Physics, Shinichi Ogawa, National Institute of Advanced Industrial Science and Technology (AIST)

2:20pm **HI+NS+TR-ThA1 Multimodal Chemical Imaging of Nanoscale Interfacial Phenomena on a Combined HIM-SIMS Platform**, ***Olga Ovchinnikova***, Oak Ridge National Laboratory **INVITED**

The key to advancing energy materials is to understand and control the structure and chemistry at interfaces. However, significant gaps hamper chemical characterization available to study and fully comprehend interfaces and dynamic processes; partly due to the lack of breadth of necessary information, as well as its scattered nature among a multitude of necessary measurement platforms. Multimodal chemical imaging transcends existing analytical capabilities for nanometer scale spatially resolved interfacial studies, through a unique merger of advanced helium ion microscopy (HIM) and secondary ion mass spectrometry (SIMS) techniques. In this talk I will discuss how to visualize material transformations at interfaces, to correlate these changes with chemical composition, and to distil key performance-centric material parameters using a multimodal chemical imaging approach on a combined HIM-SIMS system. Particular attention will be focused on how to use the HIM-SIMS to study the role of ionic migration on the photovoltaic performance, or alternatively whether the ionic migration plays a positive or negative role in determining superior photovoltaic performance in organic-inorganic perovskites (HOIPs). I will discuss how synthesizing perovskite on custom substrates effect active chemical agents in materials and understand how interfaces in materials affect the local chemistry, specifically, key energy related parameters such as electron and ion motion and their re-distribution. Overall, multimodal chemical imaging on a combined HIM-SIMS platform offers the potential to unlock the mystery of active interface formation through intertwining data analytics, nanoscale elemental characterization, with imaging; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

Acknowledgements

This work was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility

3:00pm **HI+NS+TR-ThA3 Characterizing Surface Immobilized Antibodies using ToF-SIMS and Multivariate Analysis**, *N.G. Welch*, CSIRO Manufacturing, Australia, *R.M.T. Madiona*, La Trobe University, Australia, *J.A. Scoble, B.W. Muir*, CSIRO Manufacturing, Australia, ***Paul Pigram***, La Trobe University, Australia

Antibody attachment, orientation and function at the solid interface are critical for the sensitive detection of biomolecules during immunoassays. Correctly oriented antibodies with solution-facing antigen binding regions have improved antigen capture in comparison with randomly oriented antibodies. Direct characterization of oriented proteins with surface analysis methods still remains a challenge. Surface sensitive techniques, however, such as Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) provide information-rich data that can be used to probe antibody attachment, orientation, denaturation and related characteristics.

Diethylene glycol dimethyl ether plasma polymers (DGpp) functionalized with chromium (DGpp+Cr) have improved immunoassay performance that is indicative of preferential antibody orientation. ToF-SIMS data from proteolytic fragments of anti-EGFR antibody bound to DGpp and DGpp+Cr have been used to construct artificial neural network (ANN) and principal component analysis (PCA) models indicative of correctly oriented systems. Whole antibody samples (IgG) tested against each of the models indicate preferential antibody orientation on DGpp+Cr. Cross-reference between ANN and PCA models yield 20 mass fragments associated with $F(ab')_2$ region representing correct orientation, and 23 mass fragments associated with the Fc region representing incorrect orientation. The mass fragments have been compared with amino acid fragments and amino acid composition in $F(ab')_2$ and Fc regions. A ratio of the sum of the ToF-SIMS ion intensities from the F(ab′)$_2$ fragments to the Fc fragments demonstrated a 50% increase in intensity for IgG on DGpp+Cr as compared to DGpp.

This systematic data analysis methodology offers new opportunities for the investigation of antibody orientation on a range of substrates. It also yields good results for the characterization of antibody denaturation and for determining limits of detection.

4:00pm **HI+NS+TR-ThA6 Single-nanometer Functional Graphene Devices Patterned with Helium Ion Beam**, ***Hiroshi Mizuta***, *M.E. Schmidt, T. Kanzaki*, Japan Advanced Institute of Science and Technology (JAIST), Japan, *S. Ogawa*, National Institute of Advanced Industrial Science and Technology (AIST), Japan, *M. Muruganathan*, Japan Advanced Institute of Science and Technology (JAIST), Japan **INVITED**

The bombardment of specimen by accelerated ions causes implantation and surface sputtering. The latter can be employed to create structures with sub-10 nm dimensions. This precision is demonstrated in electrically contacted and suspended graphene layers by a Helium ion microscope (HIM). 5 nm wide monolayer graphene, suspended above a pore and milled by HIM, had been demonstrated [1]. However, the physical properties of such a ribbon cannot be investigated in such a device architecture due to lack of electrical contacts. Recently, we demonstrated a ~6 nm wide suspended GNR and reported on the room temperature electrical characteristics. A wide range of drain current, at which current suppression occurs, has been observed [2]. However, that device was based on exfoliated grapheme, which makes it necessary to individually design the structures, and the yield is typically small.

Here, we report on the large-array processing of 100 nm wide monolayer CVD based suspended graphene structures by HIM. The structures are prepared by electron-beam lithography and thin-film processing. Before HIM milling, the graphene is released by buffered hydrofluoric acid etching and critical point drying. Annealing in $H_2$/Ar atmosphere is used to remove the resist contamination.

We will first discuss results of fabricating suspended GNRs with constriction milled with HIM (30 keV acceleration voltage, $1.1 \times 10^{18}$ ion/cm$^2$). The GNRs with sub-10-nm constriction are successfully patterned, and the electrical conduction is measured as function of temperature. We will discuss the milling results and electrical characterization in detail along with their potential impact on the performance of graphene-NEMS-based single-molecular detection [3]. We will then report on the recent progress in preparing arrays of nanopores in graphene by HIM. 9x9 arrays with pitch of ~9 nm are successfully realized with a dose of $6.5 \times 10^{18}$ ions/cm$^2$. Arrays of pores spanning a complete suspended ribbon with a pitch of ~18 nm are demonstrated as well, and we will discuss the impact of such periodic structure on the electrical and thermal (phononic) transport for nanoscale heat phonon engineering.

**Acknowledgements:** T. Iijima is acknowledged for the usage of the HIM at AIST SCR Station**.** This research was supported through the Grant-in-Aid for Scientific Research KAKENHI 25220904, 16K13650, 16K18090 from JSPS and COI program of the Japan Science Technology Agency.

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5:00pm **HI+NS+TR-ThA9 Monte Carlo Simulation Study of Gas Assisted Focused Ion Beam Induced Etching**, ***Kyle Mahady***, *P.D. Rack*, University of Tennessee, *S. Tan*, Intel Corporation, *Y. Greenzweig*, Intel Corporation, Israel, *R.H. Livengood*, Intel Corporation, *A. Raveh*, Intel Corporation, Israel

We present a simulation study of focused ion beam etching using a gas assist. The use of a precursor gas greatly enhances material removal rate when compared to ion beam sputtering, enabling features such as valleys to be etched with lower ion doses, and consequently less damage to the substrate. The basis of our study is a Monte Carlo based code for focused ion beam milling, which simulates the cumulative removal of material due to sputtering, and secondary electron emission, for various target compositions and structures. In this talk, we describe the gas assisted etching portion of the code, which simulates monolayer adsorption of $XeF_2$ to a $SiO_2$ substrate, and the reactions between adsorbed gas and surface atoms which lead to volatilization and material removal. We study the effect of etching parameters such as beam current and gas flux on the shape of etched valleys, and the influence of ion species such as $Ne^+$ and $Ga^+$, to characterize the underlying limitations on etching resolution. Simulations are compared against experimental results, for validation and to understand experimentally observed features.

5:20pm **HI+NS+TR-ThA10 Direct Write of Complex 3-Dimensional Structures with Helium Ion Microscopy**, ***Matthew Burch***, *A.V. Ievlev*, Oak Ridge National Laboratory, *M.G. Stanford, B. Lewis*, University of Tennessee, *X. Sang, S. Kim, J. Fowlkes*, Oak Ridge National Laboratory, *P.D. Rack*, University of Tennessee, *R.R. Unocic, A. Belianinov, O.S. Ovchinikova*, Oak Ridge National Laboratory

The next generation of computing, the generation which will follow the end of Moore’s law, will need materials processing and interconnects that exist in 3-dimensions. This need has led to multiple investigations into the fabrication of complex free standing 3-dimensional structures onto any substrate at the nano-scale. Several techniques are currently being developed to fabricate free-standing micro- and nano- level structures including two-beam photon lithography and focused electron beam induced deposition (FEBID). Recent advancements in FEBID has led to the ability to simulate and subsequently fabricate complex 3D-platinum structures from an organometallic precursor.

In this work, we demonstrate the ability of the helium ion microscope (HIM) to fabricate complex 3-dimensional structures using focused ion beam deposition (FIBID) at scales smaller than previously demonstrated with FEBID. Using modern day image analytics we demonstrate a method we’ve successfully utilize to investigate and understand some of the most important structure-growth parameters with FIBID and how that parameter space impacts the size and morphology of created structures. These parameters include beam current, organometallic gas volume, dwell time, etc., and how these impact a grown structures length, width, and possible growth angles.

We further investigate the composition and crystalline nature utilizing scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) in the prescence of different carrier gasses of nitrogen and oxygen. We show, that in general the morphology and chemistry is nearly identical between the two gasses, that there is a slight difference in the apparent crystalline nature between the two flow gasses.

Finally, we demonstrate the minimum size structures currently grown with FIBID and the complex nature of the way these structures can be grown. We also demonstrate the HIM’s unique ability to direct write structures repeatedly and reliably on non-conductive using the HIM’s unique charge compensation mechanisms.

**Acknowledgements**

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

## Manufacturing Science and Technology Group
## Room: 18 - Session MS-ThA

## Working with Government Labs and User Facilities

**Moderators:** Bridget Rogers, Vanderbilt University, Mikel Holcomb, West Virginia University

2:20pm **MS-ThA1 Tackling Fundamental and Applied Problems Using EMSL Capabilities - Examples of Applying Surface and Interface Sensitive Tools to Biological Systems**, *C.R. Anderton, D.R. Baer, M.H. Engelhard*, ***Scott Lea***, Pacific Northwest National Laboratory

Tackling many of the most difficult and pressing scientific challenges of today requires an array of advanced instrumentation and expertise. The Environmental Molecular Sciences Laboratory (EMSL) is a US Department of Energy national scientific user facility with a wide range of advanced research capabilities that provides access to users with specialized research needs. EMSL’s mission is to lead molecular-level discoveries for the Department of Energy and its Office of Biological and Environmental Research that translate to predictive understanding and accelerated solutions for national biological, energy, and environmental challenges. To achieve this goal, EMSL science is focused into four Science themes: atmospheric aerosol systems, biological dynamics and design, terrestrial and subsurface ecosystems, and molecular transformations (www.emsl.pnnl.gov). Dynamic processes that occur at interfaces underpin research in these science focus areas. EMSL provides an array of unique and advanced capabilities to facilitate interfacial research, including state of the art spectroscopy, microscopy, magnetic resonance, and computational capabilities. EMSL has also made significant strides in the development of *in situ* capabilities designed to interrogate these interfaces in real-time and in a variety of environments. By providing integrated experimental and computational resources for discovery and technological innovation in molecular sciences, EMSL particularly encourages endeavors that utilize multiple capabilities. This talk will focus attention on the application of several surface sensitive and interface tools to biological systems. Like other DOE national user facilities, access to EMSL capabilities is through a proposal and peer review process and can be no-cost for work to be disseminated to the scientific community through open literature publication. Numerous national scientific user facilities are making efforts to increase industrial utilization, and EMSL has recently taken steps to facilitate access to its capabilities for industrial users.

2:40pm **MS-ThA2 Opportunities for Users at the Center for Nanoscale Materials**, ***Kathleen Carrado Gregar***, Argonne National Laboratory

The Center for Nanoscale Materials (CNM) at Argonne National Laboratory is a premier user facility providing expertise, instrumentation, and infrastructure for interdisciplinary nanoscience and nanotechnology research. Academic, industrial, and international researchers can access the center through its user program for both nonproprietary (at no cost) and proprietary research. As a Department of Energy (DOE) funded research center, the CNM is at the forefront of discovery science that addresses national grand challenges encompassing the topics of energy, information, materials and the environment. The scientific strategy of the CNM is consolidated under the following three crosscutting and interdependent scientific themes. Collectively, they aim at the discovery and hierarchical integration of materials across different length scales, at the extremes of temporal, spatial, and energy resolutions: (a) Quantum materials and phenomena (b) Manipulating nanoscale interactions, and (c) Synthesis of nano-architectures for energy, information and functionality. Embedded within these three themes and supporting them are the vector capabilities of X-ray microscopy, electron microscopy, and computational materials science.

Unique capabilities at CNM include a premier clean room with advanced lithography and deposition capabilities, expansive synthesis and nanofabrication resources, a hard x-ray nanoprobe at the Advanced Photon Source synchrotron, myriad scanning probes including low temperature, ultrahigh vacuum STMs, TEMs with in situ holders and chromatic aberration-correction, a 30 TFlop supercomputer, and ultrafast optical probes. A key CNM asset includes outstanding staff with expertise in synthesis, nanophotonics, scanning probe and electron microscopy, nanofabrication, and theory, simulation and modeling. Core technological materials range from 2D layered materials to nanocrystalline diamond. All capabilities and expertise are available through peer-reviewed user proposals; access is free of charge for non-proprietary research. CNM is one of DOE's premier Nanoscale Science Research Centers serving as the basis for a national program encompassing new science, new tools, and new computing capabilities for research at the nanoscale (https://nsrcportal.sandia.gov). Recent staff and user research highlights will be presented, painting a picture of present and future nanoscience and nanotechnology at the CNM (www.anl.gov/cnm).

The Center for Nanoscale Materials, an Office of Science user facility, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract no. DE-AC-02-06CH11357.

3:00pm **MS-ThA3 The CNST NanoFab at NIST: *Nanofabrication for US Commerce***, *V.K. Luciani*, ***Chen Zhang***, National Institute of Standards and Technology, Center for Nanoscale Science and Technology

The NIST Center for Nanoscale Science and Technology (CNST) supports the U.S. nanotechnology enterprise from discovery to production. As part of the CNST, the shared-use NanoFab provides its users rapid access to a comprehensive suite of tools and processes for nanoscale fabrication and measurement. The CNST NanoFab at NIST is part of the Department of Commerce and therefore puts a high priority on operating a business friendly, easily accessible facility. The same rates are applied to all users, whether from industry, academia or NIST. Applications are accepted at any time and are reviewed and processed every week. Also, NIST does not claim any inherent rights to inventions made in the course of a NanoFab project. Your intellectual property rights are not affected. The NanoFab features a large, dedicated facility, with tools operated within an ISO 5 (class 100), 750 $m^2$ (8,000 $ft^2$) cleanroom and in adjacent laboratories that have superior air quality along with temperature, humidity, and vibration control. Over 80 major process tools are available, including but not limited to e-beam lithography, 5x reduction stepper photolithography, nano-imprint lithography, laser writing for mask generation, scanning and transmission electron microscopy, three Focused Ion Beam (FIB) systems, metal deposition, plasma etching, chemical vapor deposition, atomic layer deposition, deep silicon etching, ion beam etching and a soft-lithography lab. The NanoFab staff consists of scientists, engineers and technicians that specialize in all areas of nanofabrication and provide training and ongoing technical assistance to users. Our goal is to be a catalyst to our users' success and to help nurture nanotechnology commerce in the Unites States. Project applications and instructions are easily available on the web at www.nist.gov/cnst/nanofab. Users inside NIST and from all around the country are provided on-line access to tool schedules and the tool reservation system. From physicists, engineers and biologists to medical researchers, users find common ground at the nanoscale in the CNST NanoFab.

3:20pm **MS-ThA4 Research Opportunities at the Cornell NanoScale Science and Technology Facility**, ***Michael Skvarla***, Cornell NanoScale Science and Technology Facility

The Cornell NanoScale Science and Technology Facility (CNF) is a member of NNCI, a network of open-access facilities partially subsidized by the US National Science Foundation to provide researchers with rapid, affordable, shared access to advanced nanofabrication tools and associated staff expertise. Hundreds of researchers worldwide (from academia, industry, and government) utilize CNF to make structures and systems from the nanometer scale to the centimeter scale. CNF offers extensive capabilities in electron-beam lithography, stepper photolithography, soft lithography, and direct-write tools for rapid prototype development, along with the flexibility to accommodate diverse projects and to deposit, grow, and etch a wide variety of materials. CNF's technical staff is dedicated full-time to user support, providing one-on-one help with process development, tool training, and troubleshooting. They can offer expertise in a wide range of fabrication topics, including electronics, photonics, magnetics, MEMS, materials, basic studies in chemistry and nanostructure physics, fluidics, and the life sciences and bioengineering (more than 30% of CNF's users now focus on biology). All researchers are welcome and all reasonable interactions are possible; no experience in nanofabrication is necessary. A central part of CNF's mission is education and outreach, with a special interest in assisting users from "non-traditional" fields seeking assistance to implement nanofabrication techniques for the first time. CNF's user program is designed to provide the most rapid possible access (typically 2 weeks) with the lowest possible barriers to entry (users retain full control of their IP, with no entanglement by CNF or Cornell University). Projects range from extensive, long-term device development to short-term use of specific tools, advanced capabilities, or singular staff expertise.

This talk will explore the CNF tool set, areas of expertise, types of services and advice available, and examples of ongoing work with the hope of stimulating ideas and possibilities.

We invite you to explore the CNF and NNCI and discuss ways we can help bring your research visions to fruition. As a first step, CNF's User Program Managers will at no cost provide detailed processing advice and cost estimates for potential new projects. The CNF technical staff meets every Wednesday afternoon for conference calls where we welcome questions about any topic related to nanofabrication. Visit cnf.cornell.edu to contact us and get started.

4:00pm **MS-ThA6 Shyne - Allowing Users to Leverage $800 Million in Nanotechnology Research, Education, Infrastructure & Facilities at Northwestern and the University of Chicago**, ***Peter Duda***, University of Chicago, *B. Meyers*, Northwestern University

Welcome to the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource, an NSF-NNCI program! SHyNE is a new national resource that provides academic, small business and industry researchers access to cutting-edge nanotechnology facilities and expertise. In addition to traditional nanotechnology tools, SHyNE ensures the integration of soft (biological) nanostructures with the backbone of enabling hard materials, for applications such as microfluidic modules for bio-sensors and synthetic scaffolds for tissue regeneration, among others.

SHyNE streamlines our nanotechnology facilities, providing unique and integrated capabilities for internal Northwestern and UChicago researchers as well as external users, especially small and medium enterprises and startup companies. SHyNE further cements our leadership in nanotechnology and related advanced materials research, education and outreach.SHyNE deepens existing collaborations between Northwestern and UChicago and is expected to draw a variety of researchers from the Chicago area, the greater Midwest and nationally. SHyNE also offers regional colleges and public institutions, including museums, the opportunity to access research and training instrumentation under one umbrella. Through this program and the combined capabilities of the SHyNE facilities, we will connect state-of-the-art research facilities to academic, government and commercial programs across the Midwest, which in turn will lead to life-enhancing breakthroughs. As one of the 16 members of the nanotechnology network, SHyNE will benefit from and contribute to the vast resources of national collaboration of world-class peer institutions.

We wholeheartedly welcome you to use our facilities under the guidance and instruction of our talented staff, discover our unique instrumentation and capabilities, and find out more what SHyNE can do for you!

4:20pm **MS-ThA7 Science Opportunities with Soft X-Rays for Users at the Advanced Light Sources**, ***Zahid Hussain***, Advanced Light Source, Lawrence Berkeley National Laboratory

Sharper and sharper experimental tools are often crucial for understanding of novel physical phenomena and making new discoveries. Today in condensed matter physics we are experiencing need for revolutionary new instrumentation for understanding interplay of many degrees of freedom interacting at different energy, length and time scales. These interactions lead to new phases of matter and emergent phenomena such as high temperature superconductors, topological insulators and thermoelectric materials, to name a few. The primary focus of my talk is to present the science opportunity, through various examples, upon the necessity for advanced techniques and instrumentation to elucidate the application of soft x-ray synchrotron radiation for unraveling the emergent phenomena in quantum materials and energy related challenges.

4:40pm **MS-ThA8 Research Opportunities and How to Become a User at the Center for Functional Nanomaterials**, ***Samuel Tenney***, Brookhaven National Laboratory

The Center for Functional Nanomaterials (CFN) is a Department of Energy (DOE) Nanoscale Science Research Center located at Brookhaven National Laboratory. The CFN is a state of the art user facility for both proprietary and nonpropietary research with currently more than 500 users per year from industry, academia, and other government labs that publish well over 300 papers per year. The CFN is comprised of 5 research groups (interface science and catalysis, soft and bio materials, electronic nanomaterials, electron microscopy, and theory and computation) that are centered around the 3 strategic themes of the CFN including the study of Nanomaterials in Operando Conditions, Nano-architectures for Energy Solutions, and Self-assembled Nanomaterials by Design. The CFN has a very strong synergy with the National Synchrotron Light Source II (NSLS-II) and currently partners in the operation of 3 endstations that are used for the characterization of nanomaterials. The CFN houses a state-of-the-art cleanroom with world record 1 nanometer lithography capabilities among others. The CFN has over 50 staff members with expertise in a wide variety of areas related to nanoscale science that are dedicated to user support and the development and fostering of an extensive user community. Since its inception the CFN was designed with the idea of housing a complete suite of equipment, techniques, and technical staff to tackle the biggest challenges at the forefront of nanoscale science and technology all under one roof. We will also present how to become a user and discuss the process of applying for time to use the CFN's resources.

5:00pm **MS-ThA9 Opportunities at the Center for Nanophase Materials Sciences**, ***Arthur Baddorf***, Oak Ridge National Laboratory

The Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) is a DOE Office of Science User Facility that provides a national and international user community access to expertise and equipment for a broad range of nanoscience research, including nanomaterials synthesis, nanofabrication, imaging/microscopy/characterization, and theory/modeling/simulation. CNMS also acts as gateway for the nanoscience community to benefit from ORNL's neutron sources (SNS and HFIR) and computational resources. CNMS facilities are accessible based on peer-reviewed proposals and are offered at no cost to users who intend to publish their results.

In addition to a broad assortment of nanomaterials characterization tools, the CNMS has particular expertise in the following capabilities:

- Nanofabrication - The CNMS Nanofabrication Research Laboratory houses 10,000 ft2 of class 100/1000 clean room space for material modification using advanced lithographic, etching, thin-film deposition, and characterization tools.
- Bio-Inspired Nanomaterials - The CNMS offers capabilities to manipulate and image hydrated biological samples, and to create inorganic nanostructures of biological interest.
- Inorganic and Hybrid Nanomaterials Synthesis - Synthesis of nanostructures and thin films are performed by CVD and PLD with real-time diagnostics, including 2D layered materials, carbon nanostructures, oxide films, as well as hybrid organic/inorganic perovskite films, with wet/dry assembly of these materials into optoelectronic device architectures.
- Macromolecular Nanomaterials Synthesis - Laboratories include a wide range of polymer synthesis capabilities with special emphasis on selective deuteration and ionic polymerization
- Chemical Imaging – In addition to elemental distribution, bonding and chemical configuration is obtained using energy and mass spectroscopies.
- Electron and Atom Probe Microscopy - Sub-Ångstrom electron microscopy and spectroscopy, soft-matter TEM, and atom probe and electron tomographies are available.
- Scanning Probe Microscopy - Scanning tunneling and atomic force microscopies and spectroscopies in a range of environments for mapping of physical and electronic structure, electronic and ionic transport, spin, thermovoltage, electromechanics, magnetism, and dissipation.
- Nanomaterials Theory Institute - The NTI provides and advances capabilities for theory and high-performance simulation to enable fundamental understanding of physical and chemical properties of nanoscale materials.

5:20pm **MS-ThA10 Research Opportunities at the National High Magnetic Field Laboratory**, ***Eric Palm***, National High Magnetic Field Laboratory

The National High Magnetic Field Laboratory (MagLab) is the largest and highest powered magnet lab in the world. With more than 1700 users annually making use of its facilities it is a unique laboratory for basic research on topics as varied as materials, energy and life. This presentation will focus on those research capabilities as well as the technical challenges involved in creating the worlds highest magnetic fields for research.

## Nanometer-scale Science and Technology Division
## Room: 19 - Session NS+SP+SS-ThA

## Advances in Scanning Probe Microscopy
**Moderator:** Sergei Kalinin, Oak Ridge National Laboratory

2:20pm **NS+SP+SS-ThA1 Mapping Stress in Polycrystals with sub-10 nm Spatial Resolution**, ***Celia Polop***, Universidad Autónoma de Madrid, Spain, *E. Vasco, A. Perrino, R. Garcia*, Instituto de Ciencia de Materiales de Madrid, CSIC, Spain

From aircraft to electronic devices, and even in Formula One cars, stress is the main cause of degraded material performance and mechanical failure in applications incorporating thin films and coatings. Over the last two decades, the mechanisms responsible for stress generation during film deposition and processing have generated intense conjecture and scientific activity. However, no consensus has been reached so far. The main difficulty is that current models of stress generation, most of which are atomistic in nature, are only supported by data with at best sub-micron resolutions. For example, techniques such as curvature-based measurements, Raman spectroscopy, and x-ray diffraction cannot reveal the stress distribution in films on nanometer scales.

Here, we present a novel method for mapping the stress at the surface of polycrystals with sub-10 nm spatial resolution. This method consists of transforming elastic modulus maps measured by atomic force microscopy (AFM) techniques, such as force modulation method and bimodal AFM, into stress maps via the local stress-stiffening effect. The validity of this approach is supported by Finite Element Modeling simulations. By applying the method to Au polycrystalline films, we show that the intrinsic stress is heterogeneously distributed along the grain diameter, being concentrated in narrow strips adjacent and parallel to the grain boundaries (not directed inside the grain boundary, as is usually assumed). Stress gradients as intense as 100 MPa/nm are detected in these regions. Note that these gradients, which are undetectable by the standard techniques and tests used for stress analysis, are in the order of magnitude of the mechanical strengths required for many applications. The heterogeneous spatial distribution of the intrinsic stress along the grain diameter is the result of the Mullins-type surface diffusion towards the grain boundaries, and would be the probable cause of the kinetic compression that appears in polycrystals under conditions of high atomic mobility. Consequently, we demonstrate that the nanoscale stress mapping has great potential to disclose the nature and origin of the stress in solids.

[1] C. Polop, E. Vasco, A. P. Perrino and R. Garcia, "Mapping stress in polycrystals with sub-10 nm spatial resolution", submitted.

[2] E. Vasco, C. Polop, "The compressive intrinsic stress in polycrystals is not inside the grain boundary", submitted.

3:00pm **NS+SP+SS-ThA3 XTIP – A Dedicated Beamline for Synchrotron X-ray Scanning Tunneling Microscopy**, *N. Shirato, M. Fisher, R. Reininger, S.W. Hla*, ***Volker Rose***, Argonne National Laboratory

Recently, substantial progress was made on Argonne's Synchrotron X-ray Scanning Tunneling Microscopy (SX-STM) project. In particular, we demonstrated the power of SX-STM for elemental characterization and topography of individual Ni nano-islands on Cu(111) at 2 nm lateral resolution with single atom height sensitivity [1], tested a new probe tip concept based on carbon nanotubes [2], and demonstrated soft x-ray imaging of nanoscale magnetic domains of an iron thin-film by x-ray magnetic circular dichroism (XMCD) contrast [3]. Further substantial advances are expected using the new low temperature (LT) SX-STM system, which has been developed over the last 3 years and is currently under commissioning.

To fully exploit the special capabilities of the new LT x-ray microscope, XTIP, a dedicated beamline for SX-STM is under construction at the Advanced Photon Source. To meet the scientific objective of the nanoscience and nanomagnetism communities most effectively, we are going to build a soft x-ray beamline with full polarization control operating over the 500-1600 eV energy range.

The dedicated XTIP beamline will provide researchers access to a one-of-a-kind instrument. Among the potential breakthroughs are "designer" materials created from controlled assembly of atoms and molecules, and the emergence of entirely new phenomena in chemistry and physics.

This work was funded by the Office of Science Early Career Research Program through the Division of Scientific User Facilities, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant SC70705. Use of the Advanced Photon Source and the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357.

[1] N. Shirato et al., Nano Letters 14, 6499 (2014).

[2] H. Yan et al., J. Nanomaterials 2015, 492657 (2015).

[3] A. DiLullo et al., J Synchrotron Rad. 23, 574 (2016).

3:20pm **NS+SP+SS-ThA4 Kelvin Probe Force Microscopy for High-Resolution Imaging of Hydrogen in Steel Alloys**, ***Joy McNamara****, P. Korinko, M. Morgan, A. Duncan*, Savannah River National Laboratory

Understanding the mechanism of hydrogen interactions in metals is continually a topic of interest for those exploring the use of hydrogen as an alternative fuel source and for other applications which involve the long term storage of hydrogen. Atomic hydrogen in stainless steel alloys segregates to regions of extended defects, such as grain and phase boundaries, and can cause stress and premature cracking in a process known as hydrogen embrittlement. The presence of hydrogen can have serious consequences on the structural integrity and lifetime of hydrogen containers and piping, making it essential to understand the effect of hydrogen on the microstructural properties of stainless steel alloys. The migration of hydrogen through the crystal structure depends on the diffusion rate and solubility of hydrogen in a given phase which gives rise to varying hydrogen concentrations between phases. Hydrogen segregated at the surface of stainless steel specimens and particularly at defect sites changes the local work function of the material and can be measured by Kelvin probe force microscopy (KPFM). By co-locating the presence of hydrogen with extended defects at the surface using KPFM, it may be possible to predict the long term storage properties of a container. KPFM produces nanoscale surface potential (i.e., voltage) images, and is capable of measuring the local change in work function of materials with very high spacial resolution compared to current methods of optically imaging the microstructures of stainless steel. In this work, stainless steel specimens were fabricated by forging techniques and laser engineered net shaping (LENS), a directed energy deposition method of additive manufacturing, and were hydrogen charged at high pressure and temperature for approximately 2 weeks. The samples were then cut and polished to produce smooth surfaces and were imaged using KPFM. The resulting surface potential images show concentration differences of hydrogen at twin boundaries, phase boundaries and other defects as evidenced by a reduction in the local contact potential difference (CPD). Differences in CPD between the forged and LENS samples were observed and will be discussed. This work has potential to elucidate the effects of hydrogen on stainless steel components.

4:00pm **NS+SP+SS-ThA6 Video-Rate Atomic Force Microscopy**, ***Roger Proksch***, Asylum Research **INVITED**

We present results from a new, video rate AFM (Cypher VRS) capable of imaging delicate samples in air and fluid up to 625 lines/second (or >10 frames per second). This is about 300x faster than typical AFMs and 10x faster than current "fast scanning" AFMs. We will describe the architecture of this new AFM, and demonstrate the advantages of its unique design. Some recent specific examples are shown, including: (1) real time observation of the cleavage of a DNA molecule with the DNase1 enzyme. (2) a variety of high resolution examples including Bacteriorhodopsin molecules, the DNA double helix and single atomic point defects, all acquired at frame rates in excess of 1 frame per second, (3) the self-assembly of type I Collagen molecule into fibrils. Collagen molecules were injected on a bare mica surface and let spontaneously polymerize to form fibrils in a phosphate buffer. The typical banding pattern of 67 nm appeared as early as 1 min after introduction of the molecules, and, finally, (4) the dynamics of CTAB hemi-micelles at the solid-liquid interface (HOPG and aqueous buffer). These long molecules spontaneously form micelles in aqueous solutions and hemicylindrical structures upon adsorption onto HOPG. AFM can image these structures with high resolution but with the VRS the kinetics of the formation can now be followed in real time.

4:40pm **NS+SP+SS-ThA8 Novel AFM Probes Enable Highly Sensitive Chemical and Thermal Characterisation at the Nano Scale**, ***Georg Ramer****, J. Chae, S. An,* NIST Center for Nanoscale Science and Technology / University of Maryland, *V.A. Aksyuk, A. Centrone*, NIST Center for Nanoscale Science and Technology

Photothermal induced resonance (PTIR) - a hyphenated technique of optical spectroscopy and scanning probe microscopy - allows to perform chemical imaging at nanoscale resolution [1,2]. The signal generation in PTIR consists of illuminating the sample with a pulsed tunable laser and transducing the local thermal expansion using a conventional AFM tip. The rapid expansion of the sample induces a ring down motion in the cantilever with amplitudes proportional to the absorption coefficient. Absorption images can be collected by moving the AFM tip across the sample, local absorption spectra can be collected by keeping the tip still and tuning the laser. PTIR works at ambient conditions and is non-destructive, making for a wide range of possible applications.

PTIR has been successfully applied to range of different samples, from life sciences, to photonics, material science and quality control [1,2]. Recently, PTIR sensitivity down to a monolayer has been demonstrated by using optical field enhancement between a gold tip and gold substrate as well as a mechanical enhancement by resonant excitation of the AFM cantilever.

Here, we present latest advances in improving the sensitivity of PTIR. Our novel AFM tips based on a nanosized picogram scale micromechanical cantilever as a displacement sensor and an optical resonator based near field read out achieve a thermal noise limited deflection measurement in the low fm $Hz^{-0.5}$ range. Through the high sensitivity and low noise detection of these new probes we obtain PTIR spectra of monolayer samples with high signal to noise ratio, without the need for optical field enhancement or resonant excitation.

Furthermore, low detection noise across the large bandwidth achieved by these probes enables the direct measurement of the sample thermal expansion dynamics after each laser pulse. Leveraging a simple model, the fitting of the thermal expansion dynamics yields the local thermal conductivity at unprecedented, nanoscale lateral resolution.

1 Centrone, A.: 'Infrared Imaging and Spectroscopy Beyond the Diffraction Limit', Annual Review of Analytical Chemistry, 2015, 8, pp. 101-126

2 Dazzi, A., and Prater, C.B.: 'AFM-IR: Technology and Applications in Nanoscale Infrared Spectroscopy and Chemical Imaging', Chem Rev, 2016

5:00pm **NS+SP+SS-ThA9 Photoinduced Thermal Desorption Coupled with Atmospheric Pressure Chemical Ionization Mass Spectrometry for Multimodal Imaging**, ***Matthias Lorenz****, C.C. Brown,* University of Tennessee, *R. Proksch, M. Viani, A. Labuda,* Oxford Instruments, *S. Jesse, O.S. Ovchinnikova*, Oak Ridge National Laboratory

The key to advancing materials is to understand and control their structure and chemistry. However, thorough chemical characterization is challenging since existing techniques characterize only a few properties of the specimen, thereby necessitating multiple measurement platforms to acquire the necessary information. The multimodal combination of atomic force microscopy (AFM) and mass spectrometry (MS) transcends existing analytical capabilities for nanometer scale spatially resolved correlation of the chemical and physical properties of a sample surface. The combination of AFM and MS using resistively heated cantilever tips for thermal desorption has been demonstrated as a promising pathway for multimodal imaging. However, the nano-TA heated probes limit the ability to carry out more standard AFM measurements such as PFM, KPFM and cAFM. To enable a more general application of chemical imaging into an AFM platform we have developed a novel closed cell sampling on an Oxford Instruments Cypher ES for in situ surface sampling/imaging analysis using photothermal heating of the AFM tip for thermal desorption (TD) coupled to a Thermo Orbitrap Velos Pro with inline ionization by atmospheric pressure chemical ionization (APCI). This approach takes advantage of the blueTherm cantilever heating technology developed by Oxford Instruments for localized thermal desorption, and demonstrates its applicability to multimodal chemical imaging using mass spectrometry. The ability to use photothermal heating of an AFM probe versus conventional resistive heating nano-TA technology opens up the possibility for carrying out multiple AFM measurement approaches on a single AFM cantilever, for a true multimodal imaging approach to link chemical composition with material functionality. We show the use of photothermal heating as a means for thermal desorption surface sampling mass spectrometry. We illustrate the application of the AFM-MS coupling for the analysis of small molecules, i.e. pigment yellow 74 as a test substrate to show 500 nm achievable lateral resolution as well as show the application to pharmaceuticals and polymer films. Additionally, the ability to introduce fast heating rates for the TD through ps laser pulsing reduces the melting of sample material and improves the access to intact molecules.

5:40pm **NS+SP+SS-ThA11 Synchrotron X-ray Scanning Tunneling Microscopy Investigations of Magnetic and Electronic Properties of Nanoscale Metal-Clusters**, ***Hao Chang***, Ohio University and Argonne National Laboratory, *N. Shirato, M. Cummings,* Argonne National Laboratory, *H. Kersell,* Ohio University and Argonne National Laboratory, *D. Rosenmann*, *J.W. Freeland*, *V. Rose,* Argonne National Laboratory, *S.W. Hla*, Ohio University and Argonne National Laboratory

Synchrotron X-ray scanning tunneling microscope (SX-STM) [1,2] combines two of the most powerful materials characterization techniques, synchrotron X-rays and scanning tunneling microscopy. SX-STM has a great potential revolutionize material characterizations with simultaneous elemental, magnetic and topological contrast down to the atomic scale. Here, we will present our recent SX-STM results of nanoscale materials measured at the Advanced Photon Source of Argonne National Laboratory. Using SX-STM X-rays absorption spectroscopy (XAS) technique, we are able to determine the X-ray absorption cross-section of a single nickel and cobalt nanoclusters on a Cu(111) surface. By employing circular polarized synchrotron X-rays, we are also able to demonstrate X-ray magnetic circular dichroism (XMCD) of the Fe $L_2$ and $L_3$ edges of a thin iron film deposited on Cu(111) [3] as well as LSMO/LNO superlattices in room and lower temperatures. Here, polarization dependent x-ray absorption spectra have been obtained through a specially fabricated tip that captures photo-electrons. Unlike conventional spin-polarized STM, x-ray excitations provide magnetic contrast even with a non-magnetic tip. Intensity variations in the photo-excited current indicate chemical variations within a single magnetic Fe domain. Moreover, using a hard X-ray nanoprobe beamline, we have successfully detected element specific X-ray induced electron emissions from a single cobalt nanocluster at room temperature. Here, varying the incident x-ray energy across the Co electron binding K-edge enables the detection of elementally sensitive electrons. As the tip scans across the single Co nanocluster- Au(111) surface boundary, atomic spatial dependent changes in the x-ray absorption cross section are directly measured by taking the x-ray induced current as a function of x-ray energy. In addition to presenting the recent results, we will also discuss potential future research directions using SX-STM.

[1] V. Rose, K. Wang, T.U. Chien, J. Hiller, D. Rosenmann, J.W. Freeland, C. Preissner, and S.-W. Hla. ***Adv. Funct. Mater.*****23**, 2646-2652 (2013).

[2] N. Shirato, M. Cummings, H. Kersell, Y. Li, B. Stripe, D. Rosenmann, S.-W. Hla, and V. Rose. ***Nano Lett.*****14**, 6499-6504 (2014).

[3] A. Dilullo, N. Shirato, M. Cummings, H. Kersell, H. Chang, D. Rosenmann, D. Miller, J.W. Freeland, S.-W. Hla, and V. Rose. ***J. Synchrotron. Rad.*****23**, 574-578 (2016).

## Plasma Science and Technology Division
## Room: 23 - Session PS+TF-ThA

## Plasma Enhanced ALD
**Moderators:** Steven George, University of Colorado at Boulder, Mingmei Wang, TEL Technology Center, America, LLC

2:20pm **PS+TF-ThA1 Mechanical, Physical, and Electrical Properties of Plasma-Enhanced Atomic Layer Deposition of Vanadium Nitride using Tetrakis(Dimethylamido)Vanadium and Nitrogen Plasma**, ***Mark Sowa***, Ultratech, Inc., *L. Ju*, *N.C. Strandwitz,* Lehigh University, *A.C. Kozen,* US Naval Research Laboratory, *G. Zeng*, *B.A. Krick*, Lehigh University

Vanadium nitride (VN) has been proposed for a variety of thin film electronics applications including interconnect diffusion barrier and supercapacitor electrodes. As with other transition metal nitrides, VN exhibits excellent mechanical properties and has been studied for its self-lubricating coating performance. VN thin films have been created primarily through PVD methods. Recently, atomic layer deposition of VN has been reported with tetrakis(diethylamido)vanadium (TDEAV) with $NH_3$ gas and tetrakis(ethylmethylamino)vanadium (TEMAV) with $NH_3$ gas and $NH_3$ plasma.

We report plasma enhanced atomic layer deposition results for VN using tetrakis(dimethylamido)vanadium (TDMAV) with $N_2$ plasma. Optimized TDMAV pulsing and $N_2$ plasma conditions have been established. Analyses include spectroscopic ellipsometry(thickness and optical properties), four point probe(resistivity), XPS(stoichiometry and impurities), XRD(crystallinity), XRR(density and thickness), and sliding wear testing(tribological properties). Depositions were investigated over 150 - 300 °C. Sub-100 μΩ-cm resistivities have been realized at 300 °C.

2:40pm **PS+TF-ThA2 Optimizing Process Parameters for Plasma Assisted Atomic Layer Deposition**, ***David Boris***, *V.D. Wheeler,* Naval Research Laboratory, *V.R. Anderson,* ASEE (residing at NRL), *N. Nepal*, Naval Research Laboratory, *S.G. Rosenberg,* ASEE Postdoctoral Fellow, *A.C. Kozen,* ASEE (residing at NRL), *J.K. Hite, S.G. Walton,* Naval Research Laboratory, *C.R. Eddy, Jr.*, U.S. Naval Research Laboratory

Plasma assisted atomic layer deposition (PA-ALD) is a low temperature conformal layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas phase chemistry to produce varying film characteristics. The flexibility and lower growth temperatures that plasmas provide come at the cost of a complex array of process variables that often require great care on the part of the user.

In response to this challenge, this work focuses on the use of plasma diagnostics to inform the choice of process conditions for PA-ALD systems. In this work we employ optical emission spectroscopy and charged particle collectors to characterize a Fiji 200 (Ultratech/CNT) PA-ALD tool. In particular, we assess the total ion flux reaching the substrate surface and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow fractions in context of PA-ALD of AlN and $Ga_2O_3$ films. Changes in plasma parameters are then linked with changes in film characteristics.

3:00pm **PS+TF-ThA3 Tuning of Optical and Structural Properties of ZnO Deposited by Room Temperature-plasma Assisted Atomic Layer deposition**, ***Alberto Perrotta***, *J. Pilz*, *A.M. Coclite*, Graz University of Technology, Austria

Wurtzite-structured ZnO thin films have been extensively investigated because of their unique optical, electrical, and piezoelectric properties, making it the material of choice in various applications such as transparent conducting electrodes, surface acoustic wave devices, and as sensors. In engineering ZnO-based devices, the material characteristics have to meet specific requirements in terms of opto-chemical and electrical properties and crystalline structure, together with very high conformality and thickness control. Plasma-assisted atomic layer deposition (PA-ALD) has been shown able to deposit very high quality ZnO thin films, combining the low process temperature with the exceptional atomic-thickness control. Furthermore, the properties of the material can be tuned by varying the plasma characteristics, making it suitable to adapt the material to specific applications.

In this contribution, high quality ZnO thin films have been deposited by PA-ALD optimized at room temperature, adopting diethyl zinc (DEZ) and oxygen plasma. The properties of the material have been investigated as a function of the radio frequency plasma power and plasma exposure time, and characterized by X-ray diffraction (XRD), gracing incidence XRD with synchrotron radiation, spectroscopic ellipsometry (SE), and X-ray photoelectron spectroscopy (XPS). The X-ray diffraction patterns of polycrystalline ZnO thin films showed rather preferred (100) orientation and XPS analysis showed the complete removal of the DEZ carbon ligands, confirming the possibility to obtain high quality crystalline ZnO at room temperature. Furthermore, the effect of the plasma power on the opto-chemical properties, growth, and crystalline structure has been investigated. Finely tuning of the optical properties of the PA-ALD ZnO layers has been achieved, with refractive index ranging between 1.82 and 1.89 at 633 nm. Moreover, the absorption has been found to increase and shift in the visible range at low plasma power. In addition, XRD showed a distortion of the (100) peak at low and high plasma power, indicating the possibility to vary the crystallite size as a function of the plasma parameters.

As an outlook, the optimized PA-ALD process at room temperature allows the deposition of ZnO on thermo-sensitive nanostructured templates, inferring the possibility to adopt it in engineering (flexible) structured devices.

3:20pm **PS+TF-ThA4 Influence of Plasma Power on the Si Solar Cell Passivation Properties of $Al_2O_3$ Thin Films deposited by Atomic Layer Deposition at 90 °C**, *Z. Zhu*, Beneq Oy, Finland, *P. Sippola,* Aalto University, Finland, ***Emma Salmi***, Beneq Oy, Finland

In the recent years ALD $Al_2O_3$ surface passivation for Si solar cells has gained increasing popularity. The excellent passivation properties of ALD $Al_2O_3$ are based on a combined effect of chemical passivation and fixed high negative charge density. A bulk of the work has concentrated on thermal ALD, but also plasma enhanced ALD (PEALD) has been considered. However, the effect of plasma parameters, particularly plasma power, on the passivation properties remain uncharted.

In this work, we have studied the effect of plasma power on the properties of PEALD $Al_2O_3$ deposited at low temperatures with focus on the Si solar cell passivation. The $Al_2O_3$ was grown from TMA and $O_2$ plasma. All depositions were done with a Beneq TFS 200 ALD reactor at 90 °C. The lifetime was studied for as deposited and post-annealed samples.

The plasma power significantly affected the film properties. Low plasma power appeared to lead to the lowest film quality in regards of purity, density and refractive index. When the power was increased from 50 to 100–300 W the density increased from 2.6 to 2.8 g/cm$^{-3}$. Similarly, the refractive index increased from 1.61 to 1.62 (at 628 nm). The higher plasma power appeared to increase the amount of available O radicals, leading to more efficient reaction completion and improved film optical and structural properties. The same trend was also clear for the passivation properties for Si solar cells. For a 25 nm $Al_2O_3$ deposited with 50 W plasma power and annealed at 400 °C the lifetime at $10^{15}$ cm$^{-3}$ injection level was 1.1 ms, while for $Al_2O_3$ deposited with 100 or 180 W it was 2.0 ms. The interface properties were also influenced. The 50 W sample had the lowest density of negative charge and the highest interface defect density, which agreed with the lower lifetime of the sample. Interestingly, the 100 W sample had the lowest level of defect density. This can be related to the more moderate level of ultraviolet radiation from the $O_2$ plasma that the 100 W sample was exposed to as compared to the 180 W sample. Nevertheless, the 180 W sample had the best passivation properties due to its highest negative charge density. In fact, the negative charge density plays a major role in surface passivation when the magnitude of the negative charge density is much greater than that of the defect density.

High quality surface passivation of Si solar cells was achieved with PEALD $Al_2O_3$ grown at 90 °C. The passivation properties were shown to significantly improve with increasing plasma power.

### 4:00pm PS+TF-ThA6 Optimizing MoO$_3$ Plasma-enhanced ALD Thin Films for use in Controllable 2D Material Synthesis

***Brittney Burant***, MIT Lincoln Laboratory

Monolayer $MoS_2$ is a direct bandgap semiconductor with promising properties for novel devices. It has been shown that valley polarization can be achieved in $MoS_2$ monolayers with circularly polarized light, which would allow the realization of novel information processing architectures through manipulation of the valley pseudo-spin. However, current production methods of $MoS_2$ monolayers are either low yielding, or of relatively poor quality for valleytronic applications. To control the layer number, defectivity, and crystallinity of $MoS_2$, a novel method for limiting growth through the sulfurization of wafer-scale $MoO_3$ thin films has been developed.

Thorough characterization of the $MoO_3$ plasma-enhanced ALD process was performed to understand the effect of $MoO_3$ process parameters on the resultant $MoS_2$. $MoO_3$ films of 20-35 nm were deposited utilizing $(NtBu)_2(NMe_2)_2Mo$ as the organometallic precursor and $O_2$ plasma for the oxygen source. Variations in Mo precursor dose time and $O_2$ plasma exposure time show the expected trends, but substrate temperature effects are more significant. Growth per cycle increases with substrate temperature, from 0.88 Å/cycle at 100 ºC, to 1.32 Å/cycle at 350 ºC, with the highest GPC of 1.4 Å/cycle at 300 ºC. Raman spectroscopy shows that films grown at low temperature are amorphous, while polycrystalline film growth occurs above 250 ºC. These results are consistent with previously demonstrated $MoO_3$ growth utilizing the same process and precursor[1]. Surface roughness, as measured by AFM, also increases with temperature, which is consistent with a transition to polycrystalline film growth. Through XPS analysis, the deposited films were determined to be sub-stoichiometric in all deposits, averaging an O/Mo ratio of 2.6, regardless of substrate temperature.

$MoS_2$ films were grown on bare sapphire wafers by placing $MoO_3$ source wafers face-to-face with growth wafers. The wafers were oriented horizontally and enclosed in a graphite susceptor to enable inductive heating. Spacing between the $MoO_3$ source wafer and sapphire growth wafer was varied from 0 to 1 mm, and wafers were reacted at 700 ºC in $H_2S$ gas. Initial reactions have shown increasing film deposition with decreased spacing between growth and source wafers. These results suggest that $MoS_2$ film growth by this method is vapor-phase transport limited. XPS data confirms the formation of $MoS_2$ on the growth wafer, however several layers of growth are observed. The effect of $MoO_3$ source wafer crystallinity on $MoS_2$ film quality is under investigation and will be presented.

[1] Vos, M., Macco, B., Thissen, N., Bol, A., Kessels, W. *JVST A*, **2015**, 34(1), 01A103-1-7.

### 4:20pm PS+TF-ThA7 Plasma ALD of Fluorides: Process Characterization and *In Situ* Study of AlF$_3$ ALD

***Harm Knoops***, Oxford Instruments Plasma Technology, UK, *M.F.J. Vos, W.M.M. Kessels, A.J.M. Mackus*, Eindhoven University of Technology, The Netherlands

In this work we used TMA ($AlMe_3$) and $SF_6$ plasma for atomic layer deposition (ALD) of aluminum fluoride ($AlF_3$) films. $SF_6$ plasma is a novel co-reactant for ALD and we employed quadruple mass spectrometry (QMS) and optical emission spectroscopy (OES) to study the film growth. $AlF_3$ as well as other metal fluorides such as $MgF_2$ and $CaF_2$ generally have a wide bandgap (>10eV) and low refractive index (1.3-1.6). Due to these interesting properties they find use in many applications, including passivation layers in Li-ion batteries, electron transport layers in photovoltaics and protective coatings for optical devices. Previously, ALD of fluorides has been demonstrated using $TiF_4$ and $TaF_5$ as the fluorine source for the deposition of $MgF_2$, $CaF_2$ and $LaF_3$ and more recently using HF for $AlF_3$, $ZrF_4$, $MnF_2$, $HfF_2$, $MgF_2$ and $ZnF_2$.[1,2] The novel approach of using $SF_6$ plasma as a fluorine source is a promising alternative to HF, because of the ease of handling that $SF_6$ offers. Furthermore, $SF_6$ plasma provides increased reactivity at lower temperatures and allows for reduced purge times, similar to the benefits of using an $O_2$ plasma instead of $H_2O$ for metal oxide ALD.

$AlF_3$ films were prepared on Si samples over a temperature window of 50°C to 300°C. Since $SF_6$ plasma etches Si and $SiO_2$, a thin $Al_2O_3$ layer was deposited prior to $AlF_3$ growth. Using *in situ* spectroscopic ellipsometry (SE) the growth per cycle (GPC) was determined to decrease from 1.5Å at 50°C to 0.5Å at 300°C. Interestingly, no significant impurity levels of S, C and O were detected in the bulk of the $AlF_3$ films using X-ray photo-electron spectroscopy (XPS), even for low deposition temperatures. Furthermore, XPS measurements showed a F/Al ratio of 3.0±0.2. The low impurity content and the stoichiometric F/Al ratio are in line with a refractive index of 1.35 at 633nm as determined by SE.

The reaction mechanism of the ALD process was addressed based on a combination of OES and QMS. These measurements suggest that $CH_4$ is released during the TMA dosing, and that $CH_4$, $C_2H_2$, HF, and $CH_xF_y$–species are formed during the plasma exposure. Furthermore, the reaction products during the plasma exposure show different trends in their release (e.g., mostly directly after striking the plasma or peaking after a few seconds of plasma exposure), which will be used to suggest a possible reaction mechanism. In addition, consumption of F can be observed similar to what is found in etching using $SF_6$ plasma. Overall this work shows that $SF_6$ plasma is a promising co-reactant which can inspire the ALD of a wide range of metal fluorides.

[1] Pilvi *et al.*, Chem. Mater. **20** (2008)

[2] Lee *et al.*, Chem. Mater. **28** (2016)

### 4:40pm PS+TF-ThA8 Ion Energy Control During Remote Plasma ALD for Tuning Material Properties of Transition Metal Nitrides

***Tahsin Faraz***, Eindhoven University of Technology, Netherlands, *H.C.M. Knoops*, Oxford Instruments Plasma Technology, UK, *S. Karwal, M.A. Verheijen, A.A. van Helvoirt*, Eindhoven University of Technology, Netherlands, *D.M. Hausmann, J. Henri*, Lam Research Corporation, *M. Creatore, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Recently, it has been shown that the ion energy can play a significant role on the physical and chemical properties of thin films grown using plasma-enhanced atomic layer deposition (PEALD).[1] In this work, we demonstrate the impact of ion energy control during PEALD of transition metal nitrides (e.g., $TiN_x$, $HfN_x$, etc.) which are of great interest for nanoelectronic device applications owing to their low electrical resistivity and excellent diffusion barrier properties.[2] Ion energy control during plasma exposure was carried out in a commercial 200 mm remote plasma ALD system (Oxford Instruments FlexAL) equipped with radio-frequency (RF) substrate biasing (13.56 MHz, up to 100 W power, -350 V resulting DC bias voltage). In such low pressure, remote inductively-coupled-plasma reactors, the ion energy can be controlled independently of the ion flux by applying an RF bias signal on the substrate table during the plasma exposure step.

Depositions performed under no bias conditions for $TiN_x$ (at 200°C) and $HfN_x$ (at 450°C) films using a 10 s $H_2$ (+Ar) plasma yielded electrical resistivities of 1960±60 and (900±0.7)x10$^3$ μΩcm and mass densities of 3.8±0.2 and 10.1±0.2 g/cm$^3$, respectively. Enhancing ion energies with substrate biasing during PEALD was observed to have pronounced effects on the chemical composition, microstructure and material properties of these transition metal nitrides. Energetic ion bombardment through application of bias voltages lowered film resistivity by one order of magnitude for $TiN_x$ (139±10 μΩcm at -187V bias) and by two orders of magnitude for $HfN_x$ ((330±70)x10$^1$ μΩcm at -130V bias) while also increasing their respective mass densities (4.9±0.2 and 10.5±0.2 g/cm$^3$). The residual stress of these films were also observed to change from tensile under no bias to compressive under bias conditions. The oxygen impurity content for films deposited without substrate biasing (~20 to 30%) was observed to be significantly reduced (≤ 4%) in films grown with bias voltages applied during plasma exposure. Furthermore, it will be discussed how the use of substrate biasing enhances PEALD process capability by providing several additional knobs (magnitude, duration and duty-cycle of bias, etc.) for tuning a wide range of material properties.

[1] Profijt et al., *J. Vac. Sci. Technol. A*, **31**, 01A106 (2013)

[2] Karwal et al., *J. Vac. Sci. Technol. A*, **35**, 01B129 (2017)

5:00pm **PS+TF-ThA9 Understanding the Challenges in Atomic Layer Deposition of SiN$_x$ through Identification of the Surface Reaction Mechanisms**, ***Rafaiel Ovanesyan****, Colorado School of Mines, *D.M. Hausmann*, Lam Research Corporation, *S. Agarwal*, Colorado School of Mines

The rapid shrinking of semiconductor devices has created a need for the low-temperature (≤400 °C) atomic layer deposition (ALD) of highly-conformal silicon nitride (SiN$_x$) and C-containing SiN$_x$ films. However, to date, the ALD of these films remains challenging. In this work, we report the surface reaction mechanisms during the ALD of SiN$_x$ and C-containing SiN$_x$ for several ALD processes. Initially, our research focused on a baseline SiN$_x$ ALD process that used alternating exposures of Si$_2$Cl$_6$ and NH$_3$ plasma. This process was subsequently modified by replacing the NH$_3$ plasma half-cycle with a CH$_3$NH$_2$ plasma to simultaneously incorporate both C and N. Finally, to overcome the limitations of SiN$_x$ films deposited using H-containing plasmas, a three-step ALD process was developed that used Si$_2$Cl$_6$, CH$_3$NH$_2$, and N$_2$ plasma. The film composition, reactive surface sites, and adsorbed surface species were monitored using in situ attenuated total reflection Fourier transform infrared spectroscopy, which allowed us to elucidate the surface reaction mechanisms. In addition, in situ four-wavelength ellipsometry was used to obtain the growth per cycle (GPC). Ex situ analysis was used to obtain the conformality and elemental composition.

For the baseline Si$_2$Cl$_6$ and NH$_3$ plasma ALD process, our infrared spectra show that on a post-NH$_3$-plasma-treated SiN$_x$ growth surface, Si$_2$Cl$_6$ reacts with surface –NH$_2$ species to form –NH and –Si$_x$Cl$_{2x-1}$ ($x$ = 1, 2) surface species. In the subsequent NH$_3$ plasma step, the –Si$_x$Cl$_{2x-1}$ surface species are removed and the –NH$_2$ surface species are restored, allowing for the continuation of the ALD process. Film growth during the Si$_2$Cl$_6$ and CH$_3$NH$_2$ plasma ALD process occurs via an almost identical reaction mechanism, with the exception that C is incorporated in the form of -N=C=N- species during the CH$_3$NH$_2$ plasma step. In the three-step ALD process, Si$_2$Cl$_6$ again reacts with surface –NH$_2$ species, while in the CH$_3$NH$_2$ step, the CH$_3$NH$_2$ reacts with –Si$_x$Cl$_{2x-1}$ surface species via the formation of Si-N linkages to form Si$_2$N-CH$_3$ surface species. During the N$_2$ plasma step, the Si$_2$N-CH$_3$ surface species are removed and the –NH$_2$ species are restored. When we compare the GPC and conformality (see Fig. 1) of the three-step ALD process to an aminosilane and N$_2$ plasma ALD process, we observe that the three-step ALD process has a higher conformality (~90%) and a higher GPC (~0.9 Å). However, these values are less than those reported for NH$_3$- or CH$_3$NH$_2$-plasma-based ALD processes. This suggests that the three-step ALD process behaves as an intermediate between an NH$_3$- or CH$_3$NH$_2$-plasma-based ALD process and an aminosilane and N$_2$ plasma ALD process.

5:20pm **PS+TF-ThA10 First-Principles Understanding and Kinetic Monte Carlo Analysis of Reaction Mechanisms in Plasma Enhanced Atomic Layer Deposition of Silicon Nitride**, *G. Hartmann*, University of Texas at Austin, ***Peter Ventzek***, *J.P. Zhao*, Tokyo Electron America, *T. Iwao, K. Ishibashi*, Tokyo Electron Tohoku Limited, *G. Hwang*, University of Texas at Austin

Plasma enhanced ALD (PEALD) allows fabrication of high quality and ultra-conformal SiN deposition at low temperature. The PEALD of SiN films involves a repetitive two-step process of i) silicon-containing precursor adsorption/decomposition and ii) nitridation. Halogenated silanes such as hexachlorodisilane, bis(tertiary-butyl-amino)- silane, and dicholorosilane (DCS, SiH$_2$Cl$_2$) have been utilized as Si precursors and nitrogen, hydrogen or ammonia have been used as nitrogen precursors. Despite previous studies, the underlying reaction mechanisms of these Si precursors with a nitrogen containing surface during PEALD still remain uncertain. First-principles density-functional theory (DFT) calculations have been used to identify a novel mechanism for the adsorption and decomposition of DCS on a hydrogenated SiN surface. Our study predicts that the DCS adsorption and dissociation can occur by overcoming a relatively low barrier (< 0.3 eV), far lower than the prohibitively large barriers predicted for previously proposed mechanisms. Through a detailed electronic structure analysis of the reaction intermediates, we have also elucidated the principles underlying the DCS adsorption and dissociation, notably the hypervalent nature of Si which permits chlorosilanes to adsorb prior to dissociation. A proper model of the interactions between the SiN surface are necessary to explain the ALD process and also indicate the mechanism for the formation of side products, which has a considerable contribution to the thermodynamic favorability of the proposed mechanism. Insights from the first principles calculations are incorporated into a Kinetic Monet Carlo Model (KMC) to illustrate different process scenarios. Understanding these principles allows us to develop guidelines for processing conditions, such as the importance of maintaining the proper surface composition to support Si precursor adsorption and dissociation.

5:40pm **PS+TF-ThA11 *High Quality Crystalline AlN Films Produced by PEALD with Microwave ECR Plasma below 200 ºC***, ***Jesse Kalliomäki***, *V. Kilpi, T. Malinen*, Picosun Oy, Finland, *H. Enami, N. Mise*, Hitachi High-Technologies Corp., Japan, *H. Hamamura, T. Usui*, Hitachi R&D Group, Japan

Due to continuous feature size scaling down and change to the 3D structures new process innovations are now required more than ever. Conformal film formation of Al compounds such as AlN is one of the key technologies. AlN is widely used in thermal management applications and due to its compatibility with III–V compounds it has shown growing interest e.g. as interface material. There is also huge potential for AlN in MEMS manufacturing. PEALD at low temperature is one of the suitable solutions for these applications.

We have earlier reported the superiority of low pressure microwave ECR(M-ECR) plasma for Si substrate nitridation at low temperature [1]. In present study, AlN film properties were evaluated for demonstrating the advantage of the newly combined tool with the M-ECR plasma and the leading ALD system from Picosun. TMA (Trimethylaluminum) was used as Al precursor while nitrogen plasma was generated with M-ECR plasma generator to form AlN. Film properties such as density, crystallinity and conformality were studied. Composition of film was analyzed by XPS with Ar sputter.

AlN film properties were investigated as a function of deposition temperature as shown in **Fig. 1.** The film density increases with deposition temperature and at 200°C the density is 3.09g/cm$^3$, which is consistent for literature values for bulk AlN [2]. It was shown that longer N$_2$ plasma exposure time improved film density. The temperature series in **Fig. 1** shows that the growth rate was 0.57Å/c and 0.54Å/c at 100 and 250ºC, respectively. Interestingly, it was found a thickness dependent crystallization. For 20nm films deposited between 100 and 250ºC showed an amorphous structure, whereas 30nm film thickness and above show crystalline structure (verified by XRD) and higher roughness, see **Fig. 2**. Good quality films with conformality of < 0.5% (1σ non-uniformity) for 300mm wafer and high purity (C<1%, O<3%) were achieved. Efficient generation of the radicals and ions by M-ECR plasma at low pressure [3] is supposed to improve the film properties.

The step coverage obtained in this study at AR 1:20 is >90% as shown in **Fig. 3.** This is promising for 3D device fabrication where conformal coating of high aspect ratios is crucial. From these results, PEALD with M-ECR plasma can be one of the most advantageous solutions for next generation devices and opens the possibilities for beyond-silicon CMOS devices.

[1] H.Hamamura *et al.*, 16th International Conference on Atomic Layer Deposition (ALD2016)

[2] JCPDF 00-003-1144 (AlN)

[3] H.Enami *et al.*, submitted to ALD2017

## Plasma Science and Technology Division
## Room: 22 - Session PS+VT-ThA

## Plasma Diagnostics, Sensors and Control

**Moderator:** Aranka Derzsi, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Hungary

2:20pm **PS+VT-ThA1 Quantitative Analysis of Composition and Temperature of Semiconductor Processing Plasmas via Terahertz Spectroscopy**, ***Yaser Helal***, *C.F. Neese, F.C. De Lucia*, The Ohio State University, *A. Niabati, M. Johnson, B. Craver, P.J. Stout, M.D. Armacost*, Applied Materials, Inc.

Processing plasmas are at a similar pressure and temperature to the environment used to study atmospheric and astrophysical species in the terahertz (THz) spectral region. Many of the molecular neutrals, radicals, and ions present in processing plasmas have been studied in the laboratory and their absorption spectra have been cataloged or are in the literature for the purpose of astrophysical study. Recent developments in THz devices have made technology commercially available for applications outside of specialized laboratories. The methods developed over several decades in the THz spectral region for these laboratory studies are directly applicable to diagnostic measurements in the semiconductor manufacturing industry. In this work, a continuous wave, intensity calibrated THz absorption spectrometer was developed as a remote sensor of gas and plasma species. A major advantage of intensity calibrated rotational absorption spectroscopy is its ability to determine absolute concentrations and temperatures of molecular species from first principles without altering the plasma environment. An important part of this work was the design of the optical components which

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*** TFD James Harper Award Finalist**

couple 500 – 750 GHz radiation through a commercial inductively coupled plasma (ICP) chamber. The measurement of transmission spectra was simultaneously fit for background and absorption signal. The measured absorption signal was used to calculate absolute densities and temperatures of polar species. Examples of measurements made in ICPs will be presented. Also, time resolved measurements were made and the time evolution of molecular densities will be discussed.

2:40pm **PS+VT-ThA2 *In Situ* Measurement of Electron Emission Yields from Plasma-Exposed Surfaces**, ***Mark Sobolewski***, National Institute of Standards and Technology

Surfaces exposed to plasmas are bombarded by energetic particles which may induce electron emission. The emitted electrons may in turn influence the plasma. Accurate plasma simulations require knowledge of the flux or yields of emitted electrons. Yields can be measured directly in beam studies, but it is impractical to produce a beam of each possible energetic particle that could be produced by typical plasmas. In contrast, in-situ measurements, performed during plasma exposure, may provide useful values or bounds for effective or total electron emission yields, summed over all (or some subset) of the energetic particles present for given plasma conditions. Here, measurements were performed at 10 mTorr (1.3 Pa) in an inductively coupled plasma system equipped with an electrostatic shield and variable-frequency rf substrate bias. An insulating cap is placed on the rf-biased electrode to minimize edge effects. The cap also reduces the effective electrode size, which further limits any undesired effects of rf bias on the plasma and allows yield measurements on small substrates. The rf voltage and current across the sheath adjacent to the rf-biased electrode are measured and analyzed by detailed, numerical sheath models, which allow the current of electrons emitted from the surface to be distinguished from other mechanisms of current flow. The observed dependence on voltage and rf phase allows some discrimination between emission induced by energetic positive ions and that induced by photons and metastables. The technique is validated by comparing measurements made in argon discharges with literature results from beam studies and then is applied to plasma etching discharges in fluorocarbon gas mixtures.

3:00pm **PS+VT-ThA3 Studying Dynamic and Structured Plasma Systems Utilizing Laser-Collision Induced Fluorescence**, ***Edward Barnat***, *A. Fierro*, Sandia National Laboratories **INVITED**

Laser collision-induced fluorescence (LCIF) is a powerful diagnostic which can be used for making temporally and spatially resolved measurements of electron densities in a plasma discharge. The technique, which involves the measurement of optical emission emanating from higher energy excited states due to the redistribution of the lower energy laser-excited state by collisions with energetic plasma species, has been readily employed to study both helium and argon discharges. In this presentation, an overview of the fundamental principles and anticipated limitations of the LCIF method will be presented. Examples of the LCIF method applied to structured and dynamic discharges generated in helium and argon will be presented to demonstrate the utility of this diagnostic technique. Finally, recent efforts used to extend the LCIF method to higher pressure (near atmospheric pressure) discharges will be discussed.

4:00pm **PS+VT-ThA6 Effect of Ion Inertia on Ion Energy Broadness on Biased Electrode in Dual Frequency Capacitively Coupled Argon Plasma**, ***Yunchang Jang***, *H.-J. Roh, N.-K. Kim, S. Ryu, G.-H. Kim*, Seoul National University, Republic of Korea

Ion response time to RF sheath voltage is important to control the energy spread of ion energy distribution (IED) in the dual frequency capacitively coupled argon plasma. IED is known as being governed by the dynamics of ion in RF sheath and the magnitude of RF voltage peak. In previous study, semi-analytic models to determine IED were derived from concept of ion response time ($\tau_i$). Ion energy broadness ($\Delta E_i$) was represented in terms of the sheath voltage oscillation ($V_{pp}$) and $\tau_i/\tau_{rf}$. Ion response time was assumed as ion transit time across the sheath, $\tau_{ion}$ by adopting correction factor without thorough understanding. In this study, we investigate the underlying physics of the correction factor, consequently defining the ion response time $\tau_i$ with RF sheath voltage oscillation. Experiment were performed in dual frequency CCP at 20 mTorr of argon gas which has the ratio of maximum sheath size to ion mean free path ~ 2. Various ranges of RF bias (from $\tau_{ion}/\tau_{rf} \sim 0.05$ to $\tau_{ion}/\tau_{rf} \sim 10$) were applied to bottom electrode to enhance the incident ion energy with very high frequency (VHF, $\tau_i/\tau_{rf} \sim 10$) applied on the top electrode (showerhead) to sustain plasma. A commercial retarding field analyzer (Impedans, Vertex V4.0.10) was employed to measure IED. Plasma density, electron temperature and plasma potential were measured by using RF compensated Langmuir probe. Experimental results of $\Delta E_i$ to $V_{pp}$ were compared with models under assumptions that ion response time is ion transit time across the sheath ($\tau_{ion}$) or one of ion plasma frequency ($1/\omega_{pi}$). Experiment results revealed that the time scale of ion response time is determined by $1/\omega_{pi}$ rather than $\tau_{ion}$ in this high-density plasma. This result implies that ion response time is governed by the ion inertia at the sheath boundary to RF sheath oscillation. Ion inertia becomes the initial condition of ion acceleration and govern the ion energy arriving at surfaces.

4:20pm **PS+VT-ThA7 Collision Frequency Estimation using Microwave Hairpin Resonator Probes**, *D. Peterson*, ***Steven Shannon***, North Carolina State University

Microwave hairpin resonator probes have become convenient alternatives to Langmuir probes to measure electron density in low temperature plasmas. The impact of electron collisions with neutrals with regard to the analysis of the resonant frequency shift from which this density is determined has been well established.[1] In this work, a method for extracting the electron neutral collision frequency by measuring resonance broadening due to collisions is presented. By using both the resonance frequency and collision-broadened resonance width, the electron density and electron neutral collision frequency can be measured. Measurements are made in argon, oxygen, $Ar/O_2$, and helium plasmas sustained in an RF driven capacitive coupled parallel plate system operating in the 100's of mTorr to Torr range. Comparisons to calculated and modeled collision frequencies in single component background gases (Ar and He) are made; experimental results agree well with these conditions. Collision frequency measurements in more challenging regimes including molecular gases and gas mixes are also presented to demonstrate applicability across a broad range of pressures and gasses. Probe design, analysis methodology, and parametric trends in capacitive systems with regard to gas density, electron density, power density, and gas composition will be presented. This work is supported through a generous gift by Applied Materials Inc.

[1] *Plasma Sources Science and Technology* 16, no. 4 (2007): 716

4:40pm **PS+VT-ThA8 In-Situ Diagnostics of Processing Plasma and Semiconductor Films for High-Efficiency Silicon Hetero-Junction Solar Cells**, ***Shota Nunomura***, National Institute of Advanced Industrial Science and Technology (AIST), Japan **INVITED**

The plasma processing is a key technology for fabricating semiconductor devices such as solar cells, light-emitting diodes and transistors. In those devices, the semiconductor films are often prepared and/or post-processed by various plasma processes. During the processes, the films are exposed into the UV, radicals, and ions, and thereby the electronic property of the films is often degraded. So, the investigation of the plasma-material interaction is important for understanding the degradation mechanism and also for further developing the plasma processing technology.

Here, we show in-situ characterization of the electronic property of semiconductor films as well as the gas-phase plasma diagnostics during the plasma process. The process we diagnosed was PECVD of hydrogenated amorphous silicon (a-Si:H) for the passivation of silicon heterojunction solar cells. The plasma parameters and gas-phase spices, such as ions, radicals, and precursors are measured by using conventional techniques of Langmuir probe, quadrupole mass spectroscopy and optical emission spectroscopy [1-3]. Together with this gas-phase diagnostics, we measured the transport properties of the growing a-Si:H films such as carrier transport and trapping, by using a recently developed optical pump probe technique [4,5]. The optical property such as the bandgap, refractive index and extinction coefficient, was also characterized by real-time spectroscopic ellipsometry.

We found that transport property of the a-Si:H films was strongly limited by the defects generated during the PECVD process, and improved by post-deposition annealing process. The generated defects were distributed near the film surface; the defect rich surface layer was estimated to be less than approximately 10 nm. As for defect annihilation, the post deposition annealing was very efficient. The annealing temperate and period strongly influence the defect relaxation, inducing the improved carrier transport. The relation between the plasma process and transport property will be described in the presentation.

[1] S. Nunomura, I. Yoshida, and M. Kondo, *Appl. Phys. Lett*. **94**, 071502 (2009). [2] S. Nunomura and M. Kondo, *J. Appl. Phys.* **102**, 093306 (2007). [3] S. Nunomura. H. Katayama I. Yoshida, *Plasma Sources Sci. Technol.* **26**, 055018 (2017). [4] S. Nunomura, I. Sakata, and M. Kondo, *Appl. Phys. Express* **6**, 126201 (2013). [5] S. Nunomura and I. Sakata, *AIP Advances* **4**, 097110 (2014).

5:20pm **PS+VT-ThA10 Towards *In Situ* Microwave Imaging in Plasmas**, *A. Tselev*, University of Aveiro, Portugal, *J. Fagan*, NIST, ***Andrei Kolmakov***, CNST/NIST

There exists a great need for *in situ* nanoscale characterization of surface/interface morphologies during plasma treatments. These include plasma induced growth, surface modification, sputtering and other processes relevant to semiconductor and aerospace industries, environmental remediation and biomedical applications. To address these needs, the current approaches rely on either "post mortem" sample microscopy or *in situ* optical analytical methods. The latter, however, lack required nanoscale spatial resolution.

In this communication, we propose to use near-field microwave imaging known as scanning Microwave Impedance Microscopy (sMIM) to image processes in plasma. Different to optical microscopy, the sMIM is sensitive to variations of local permittivity and conductivity of the material under a scanning probe. We demonstrate applicability of the sMIM to monitor plasma-assisted processes with a submicron spatial resolution. In our approach, a plasma environment with an object of interest is separated from the sMIM probe and the rest of the microscope by a SiN membrane of a few-10s nm thickness, and the imaging is performed through this membrane. As a proof of concept, we were able to image carbon nanotube films drop-casted onto the SiN membranes and their transformations in the process of plasma-induced oxidation by a low-pressure air plasma. To the best of our knowledge this is the first report on application of an SPM for in situ imaging of plasma processing. The experiential limitations such as electromechanical and thermal stability of the membranes will be discussed.

5:40pm **PS+VT-ThA11 Probe System for Radical Species Characterization in Vacuum with Centimeter Spatial Resolution**, ***Ivan Shchelkanov***, *D. Qerimi, A. Hayes, J.T. Wegner, D.N. Ruzic*, University of Illinois at Urbana-Champaign

Among plasma diagnostics one of the most difficult tasks is getting an estimate of radical gas species concentration in the ground state without plasma presence in the diagnosed volume. This is probably the major task for characterisation of downstream plasma composition in various areas of applied plasma technology and the requirements for characterisation tool are very strict. The ultimate device should have a good spatial resolution, relatively high response time, operate in highly reactive plasmas and in presence of sputtering flux materials, should be capable to characterize species of unknown geometrical distribution and composition.

The idea of a tool, which could satisfy most of the mentioned requirements, was proposed more than ten years ago [1] but only recently the Center for Plasma Materials Interaction was able to develop a complex system which can measure composition and density of radical species with 1 cm spatial-resolution and response time of 15 seconds in the presence of high intensity RF fields and flux of sputtered material. The system can measure density of oxygen, nitrogen, and hydrogen radicals, when different species present in the chamber at the same time. For vacuum chamber of 13 inch in diameter and 46 inches tall, which is equipped with 1 kW Helicon plasma source , the measured density at ~75 mTorr, 1kW power and 10 inch from the source, the density of radical species of hydrogen was 0.7 [±0.5] $*10^{21}$ $m^{-3}$ and of nitrogen radicals it was 1.1 [±0.7] $*10^{20}$ $m^{-3}$. Additional comparison with zero dimensional model showed a match with-in an errorbar between an experiment and the model.[2]

The principle of the radical species concentration measurement is the following. The thermocouple tip is coated with a particular catalytic metal. Once the probe is exposed to the gas atoms, recombination of gas atoms occurs on the surface of the probe tip. The catalytic surface provides efficient recombination thus more energy is delivered to the surface from the recombination reaction [3] compared to a probe tip without the catalytic surface. By measuring the temperature of the probe it becomes possible to quantify the amount of gas atoms in the probe vicinity. Different radical species can be distinguished by using catalytic surfaces particular to the species in question. Current work is focused on radical probe system capabilities, physical limitations, and examples of characterized plasmas.

**References:**

1. M. Mozetic / Vacuum V.47 #6-8 pages 943 to 945 (1996)

2. D.T. Elg / *J. Micro/Nanolith. MEMS MOEMS, 16, 023501 (2017)*

3. M. Mozetic / Surface & Coatings Technology 201 (2007) 4837–484

6:00pm **PS+VT-ThA12 Spatiotemporal Evolution of RF Magnetic Field and Plasma Current in a Very High Frequency Plasma Source**, ***Jianping Zhao***, *P.L.G. Ventzek, B. Lane, C. Campbell,* Tokyo Electron America, *T. Iwao, K. Ishibashi*, Tokyo Electron Limited

Large-area plasma processing systems capacitively driven at very high frequencies (VHF, e.g. 100MHz) have attracted much interest for semiconductor device and flat panel display processing. VHF has the advantage of generating plasma with more efficiency as power is coupled more into electrons and less into ions in the sheath. Benefits are seen for processes requiring reduced ion bombardment energy, ostensibly to minimize damage, high ion and radical flux to the substrate. The benefits of VHF are accompanied by challenges. The short wavelength associated with VHF source power is reduced even further in the presence of high density plasma. The wavelengths are comparable to the RF electrode dimension. High plasma densities can also lead to skin effects that screen the electromagnetic fields from parts of the plasma. As a result, spatial variations in plasma density and sheath voltage can arise and lead to undesired non-uniformities in process parameters such as etch or deposition rate. E to H transitions and plasma-sheath local resonances are other potential destroyers of plasma uniformity. Resonances and mode jumping can potentially prevent smooth plasma property control through adjustable process parameter changes. In order to understand these fundamental electromagnetic effects on VHF plasma non-uniformity to achieve a better design of plasma source, it is desired to have a detailed investigation on the spatial and temporal evolution of RF magnetic field and plasma current spanning a large RF power, pressure, and chemistry range. We present here a time and phase resolved measurements of the spatial structure of the electromagnetic waves in a 100MHz plasma source performed with a magnetic field probe (B-dot loop). The probe was translated across the diameter of the VHF plasma, measuring the magnitude and phase of the fundamental and harmonics of the plasma excitation frequency as a function of radial position. The measured magnetic fields displayed a transition from simple to complex behaviors depending on plasma conditions. The spatiotemporal resolved magnetic field exhibits a series of fast current reversal and subsequent circulation driven by inward wave propagation that are electromagnetic in nature. We show how the onset, frequency and amplitude of the current reversal and subsequent circulation are strongly related to applied plasma conditions (e.g., density, sheath thickness). We also show that plasma current derived from the magnetic field distribution is closely correlated to the plasma density profile measured by a plasma absorption probe.

## Surface Science Division
## Room: 25 - Session SS+AS+EM-ThA

### Semiconductor Surfaces
**Moderators:** James Ohlhausen, Sandia National Laboratories, Petra Reinke, University of Virginia

2:20pm **SS+AS+EM-ThA1 Visualizing the Nanoscale Electrostatics of Material Interfaces**, ***Vincent LaBella***, SUNY Polytechnic Institute, *W. Nolting*, University at Albany, SUNY **INVITED**

Electrostatic barriers at material interfaces are the foundation of electronic and optoelectronic devices. Their nanoscale uniformity is of paramount concern with the continued scaling of devices into the sub 10 nm length scale and the development of futuristic nanoscale devices. This creates a fundamental and technological need for nanoscale insight into the fluctuations of electrostatic barriers at material interfaces. This presentation will focus on our development of visualizing the nanoscale electrostatic fluctuations that are occurring at metal-semiconductor and metal-insulator-semiconductor interfaces. This is accomplished by acquiring tens of thousands of ballistic electron emission microscopy spectra on a grid and fitting them to get the local Schottky barrier height. Both false color images as well as histograms of barrier heights are then created and compared to theoretical modeling. This has given new insight into both the scattering of the hot electrons and the interface composition and their effect on the electrostatics. For example, interfaces with incomplete silicide formation and mixed metal-species interfaces have been imaged and when combined with cross-sectional TEM provide new insight into their effects on the electrostatics that is not possible with conventional bulk transport measurements or other metrology techniques.

3:20pm **SS+AS+EM-ThA4 Reactions of Benzoquinone with Hydrogen Terminated Silicon Surfaces**, ***Meixi Chen***, *J.H. Hack, A. Iyer, R.L. Opila*, University of Delaware

Iodine and Quinhydrone(QHY) dissolved in methanol have long been known to react with hydrogen terminated silicon surfaces to passivate electronic defects where photo-excited carriers recombine non-radiatively. The mechanism of this passivation is not well understood. The two constituent parts p-benzoquinone(BQ) and hydroquinone(HQ) have been studied separately in this work. We have shown that even though BQ and HQ are a redox couple, they behave very differently in reacting with silicon surfaces. The reaction is photolysis, pH sensitive and solvent-dependent. X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry were used to show that the BQ reacted with the surface. The electrical passivation of silicon surfaces is confirmed by carrier lifetime measurements where the silicon surface recombination velocity is deceased to 11cm/s. Changes in surface band bending are observed in XPS surface photovoltage. DFT calculations have also been performed. The reaction mechanism will be discussed in detail.

4:00pm **SS+AS+EM-ThA6 Uniform Reactivity and Bonding between Si(100) and GaAs(100) Wafers using Low Temperature (<180°C) Wet NanoBonding™ Optimized by Surface Energy Analysis**, ***Nicole Herbots***, *R. Islam*, Cactus Materials

Bonding two semiconductors surfaces such as Si and GaAs can increase performance in solar cell efficiency and high power electronics. In this work, the surface chemistry and topography of Si and GaAs are investigated to optimize the bonding of the pair. A new process called Nano-bonding™ [1,2 ] can nucleate cross-bonding molecules via electron exchange between two surfaces into a macroscopically continuous bonding "inter-phase" . The surfaces to be bonded are first chemically smoothed at the nano-scale and then terminated with matching "precursor phases". When activated, these phases exchange electrons. In other words, one surface is prepared so that it interacts preferentially with electron acceptors while the other surface is prepared to preferentially interact with electron donors. Hence, the precursor phases must be stable in air at room temperature until the surfaces are put into contact in clean-room class 10/ISO2 conditions and at low temperature (< 180°C). To bring the two surfaces into uniform contact while activating electron exchange and cross-bonding reactions, isotropic steam pressurization is applied, hence the name "Wet" Nano-Bonding™ [1,2].

The precursor phases are optimized based on insights provided by the Van Oss theory, combined with characterization of composition via Ion Beam Analysis (IBA), with surface energies via Three Liquids Contact Angle Analysis (3LCAA) and with surface topography using Atomic force Microscopy. On smooth surfaces, the Van-Oss theory separates contributions to the total surface energy $\gamma^T$ into molecular interactions $\gamma^{LW}$, and interactions with electrons donors $\gamma^+$ and acceptors $\gamma^-$. These can then be each extracted accurately from 3LCAA measurements [2] using multiple (>3) drops. NanoBonding™ is observed when surface pairs complement each other for electron exchange: one surface with high $\gamma^+$ and the other with high $\gamma^-$ leads to the formation of molecular cross-bonds. However, IBA and 3LCAA characterization results show that this criteria is not sufficient. The total surface energies $\gamma^T$ for both GaAs, and Si must be larger than 40 mJ/m$^2$. This is due to the fact that the contribution of interactions with electron donors and acceptors needs to amount to at least 10-15% of $\gamma^T$, so that total surface interaction $\gamma^T$ is not mostly controlled by molecular interactions $\gamma^{LW}$ , but exhibits significant non-molecular interactions with both acceptors and donors. Only then can the dominance of interactions with acceptors on one surface and interaction with donors on the other surface promote NanoBonding™ effectively.

[1] Herbots N. et al. US Patent 9,018,077 (2015); 9,589,801 (2017).

4:20pm **SS+AS+EM-ThA7 Evaluation of Silicon Oxidation in Downstream Plasma Photoresist Strip with Reducing Chemistries**, ***Tongchuan Gao***, *V. Vaniapura*, Mattson Technology, Inc.

With the rapid development of ultra-shallow junction depth devices, minimized silicon surface damage with the photoresist (PR) strip processes is stringently required. Silicon oxidation associated with the strip processes results in silicon loss, and, therefore, adversely affects the source-to-drain current of the devices. This leads to an ongoing effort to develop strip processes with both high PR ash rate and low silicon oxidation rate. The commonly used PR removal technique, downstream oxidizing chemistry plasma, may result in significant silicon surface oxidation. Recently, reducing chemistry has been extensively investigated for PR stripping with very low silicon surface damage.

To understand the silicon oxidation behavior with PR removal using reducing chemistries, a series of experiments were conducted. Silicon wafers with controlled pre-processing native oxide thickness were treated in an inductively coupled plasma downstream reactor with different reducing chemistries. Processes with different reducing chemistry composition, plasma source power, processing time, and post-processing queuing time were systematically studied. Comparison was also made between reducing and oxidizing chemistries. The oxide growth was reduced by tuning the reducing chemistries as well as the hardware configuration. Ellipsometry and X-ray photoelectron spectroscopy (XPS) were used for oxide thickness measurement and quantitative chemical composition analysis for the pre- and post-processing wafers, respectively.

The experimental results demonstrated that higher $H_2$ content in the chemistry leads to more oxide growth, which may be attributed to that energized hydrogen species break the Si-Si bonds and then oxidation takes place, or that hydrogen can penetrate the silicon substrate and then are replaced by oxygen. Time-dependent oxidation tests showed that the oxide growth rate is higher for silicon wafers with thinner pre-processing native oxide layer due to the self-limiting nature of oxide growth. Most of the oxide growth happens within the first 30 seconds of the processes. PR ash rate and uniformity were monitored correspondingly to ensure satisfactory PR removal. Our work sheds light on the optimization of reducing chemistry plasma processes for efficient PR removal with minimal silicon oxidation.

4:40pm **SS+AS+EM-ThA8 Surface-sensitive Measurement of Dielectric Screening via Atom and Electron Manipulations**, ***Daejin Eom***, *E. Seo*, *J.-Y. Koo*, Korea Research Institute of Standards and Science, Republic of Korea

Dielectric screening is essential in determining semiconductor properties. Its assessment on the surface, however, is beyond the capability of conventional capacitance and optical techniques due to their lack of surface sensitivity. Here we present the surface-sensitive measurement of the dielectric screening by using the scanning tunneling microscopy and spectroscopy. To be specific, we generate a single-atom defect on the surface and vary its ionization state by a single-electron charge. We then assess in-plane dielectric constant and Debye length at the surface by probing the surface potential modulation with atomic resolutions. Such single-atom and single-electron manipulations on B $\delta$-doped Si(111) surface unravel that the dielectric screening on this surface is much in excess of what the classical image-charge model predicts, which we ascribe to the strained bonds and the ionic character of the surface layers. Also, as an exemplary application of the measured screening parameters, we demonstrate determining the ionization state of a surface defect from the defect-induced band bending.

5:00pm **SS+AS+EM-ThA9 The Effects of UV Irradiation, Stage Temperature, and Radical Flux on UV-Ozone Treatment using High-aspect-Ratio Cave Structures**, ***Shogo Uehara***, *T. Sugawara*, *P. Wood*, SAMCO Inc.

UV-ozone treatment provides an atomic oxygen chemical reaction, where oxygen radicals are produced by UV-induced or thermal dissociation of ozone. Previously, it was found that ozone flux and stage temperature were critical for wettability improvement of polymer substrates such as polyetheretherketone (PEEK) [1]. However, in that study, the effects of UV irradiation, temperature, and oxygen radical flux were not clearly distinguished. In this research, a cave structure was employed to better elucidate the reaction mechanisms of UV irradiation, substrate temperature, and radical flux in UV-ozone treatment.

Polyimide-coated and photoresist-coated silicon coupons (5 mm x 5 mm) were placed at various depths inside a straight aluminum cave (6 mm x 6 mm square and 96 mm maximum depth). A SAMCO model UV-2 was used for this study. This system employs a cold cathode, mercury vapor UV lamp (185 nm and 254 nm), a remote (ex-situ) silent discharge high-concentration ozone generator (30-160 g/m$^3$) and sample stage heating (50 to 200°C). The surface wettability of polyimide was examined using the water contact angle, and the photoresist ashing rate was measured using a stylus profilometer (Ambios Technology, XP-200).

Generally, samples placed at higher aspect ratios showed higher contact angles and lower ashing rates. This indicated that the reactive species were deactivated or did not reach the sample when the aspect ratio became larger (i.e. the depth of the sample in the cave became greater). At an aspect ratio of 15, with ex-situ ozone only (no UV irradiation) and a stage temperature of 100°C, the polyimide samples did not show a significant ashing rate or contact angle decrease. However, at 200°C, the samples processed with ex-situ ozone only (no UV irradiation) showed contact angle of 15.40° against the initial value of 93.70° and an ashing rate of 9.95 nm/min. The samples processed using UV irradiation with ex-situ ozone at 200°C showed a contact angle of 75.93° and an ashing rate of 7.67 nm/min.

From these results, it was concluded that production of oxygen radicals was accelerated by thermal dissociation of ozone at the higher temperature. The oxygen radical flux produced at high temperature gradually decreased in the cave as the aspect ratio became greater, but it remained relatively high and caused temperature-driven surface chemical reactions. It was postulated that the 254 nm UV irradiation dissociated ozone that otherwise would have reached deep inside the cave and thermally dissociated [2].

[1] Uehara, S., Kawabe, T., Wood, P., & Tsuji, O. (2016). *MRS Advances*, **1**.11, 743-748.

[2] Wood, P., Wydeven, T., & Tsuji, O. (1993). *MRS Proceedings*, **315**. 237.

5:20pm **SS+AS+EM-ThA10 Density Functional Theory Study of the Effects of Surface Defects on the Interactions of Cl and α-$Fe_2O_3$ (0001) Surface**, ***Qin Pang***, *H. DorMohammadi*, *O.B. Isgor*, *L. Árnadóttir*, Oregon State University

Fe (III) oxides are the dominant structure of the outer layer of the iron passive film formed in alkaline environment, but chloride ions have been shown to induce depassivation of these passive films under the same conditions. Here we use hematite (α-$Fe_2O_3$) to represent the Fe (III) oxides and DFT+U method to investigate the mechanism of the depassivation by studying the interactions of Cl with both pristine α-$Fe_2O_3$ (0001) surface and the surface with defects. Total of four surfaces are considered, pristine surface, Fe vacancy surface, O vacancy surface and Fe-O pair vacancy surface. We found that the O vacancies have a positive effect on the adsorption of Cl on the surfaces while the Fe vacancy has a negative effect. The strength of the adsorption on the same site on the four surfaces can be ranked as O vacancy surface, Fe-O pair vacancy surface, pristine surface and Fe vacancy surface. The insertion of the Cl into the sub surface was studied on the four surfaces as well and was found to be endothermic for all four surfaces but surface defects have positive effects on the insertion of Cl by making it less endothermic. The insertion reaction is less endothermic on the O vacancy surface and Fe-O pair vacancy surface. On these two surfaces, the Cl insertion process goes through an O vacancy with reaction energy around 0.5 eV, which is about 1 eV lower than the reaction energy on the pristine surface. The Cl insertion energy is slightly coverage depended, but the insertion remains less favorable than the adsorption of Cl even at higher coverages.

## 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 $\rho$ 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$_2$O$_3$ Nanolaminates on Single-crystal GaN and Ga$_2$O$_3$: 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$_2$O$_3$ NLs on Si (with native SiO$_2$ layer) substrates and then on both GaN and Ga$_2$O$_3$ single crystals. A variety of samples ranging from their homogeneous mixtures to HfO$_2$ or Al$_2$O$_3$-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$_2$O$_3$)-NL interface. By quantifying the HfO$_2$ incorporation throughout the Al$_2$O$_3$ layer and using the programmable nature of ALD to alternate layers of the HfO$_2$ and Al$_2$O$_3$ in an $(AB)_x$-$(CD)_y$ fashion, the influence of HfO$_2$ mobility within Al$_2$O$_3$ 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$_2$O$_3$)-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

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*** TFD James Harper Award Finalist**

$BiFeO_3$ (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 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.

## Vacuum Technology Division
## Room: 9 - Session VT-ThA

## Surface Science for Accelerators
**Moderators:** Jay Hendricks, NIST, Alan Van Drie, Tri Alpha Energy, Inc.

2:20pm **VT-ThA1 Adsorption/Desorption from Amorphous Carbon Coating at Cryogenic Temperatures**, ***Anne-Laure Lamure***, *V. Baglin, P. Chiggiato, B. Henrist*, CERN, Switzerland **INVITED**

The CERN Large Hadron Collider (LHC) is the world's biggest particle storage ring. Particles circulate in a 27km pipe, under vacuum. One of the main vacuum limitations is the electron cloud.

Photoelectrons are produced when the synchrotron radiation from the proton beam hits the wall. They are then accelerated toward the beam, gain energy and extract new electrons by secondary electron emission. The avalanche phenomenon which is observed is called multipacting.

Electron cloud is deleterious as it interacts with the beam, induces gas desorption and produces additional heat load on the cryogenic system of the magnets.

In order to mitigate the multipacting effect for the upgraded LHC (HL-LHC), amorphous carbon, with a low secondary electron yield, will be coated in some cryogenic magnets.

In this context, it is important to know the behaviour of the usual residual gas (H2, CO, CH4, CO2) on amorphous carbon coating held at cryogenic temperature, in order to know how to operate the vacuum in the accelerator. The quantity of gas that can be stored on the surfaces and the binding energy of adsorption are two highly interesting information.

The results of two types of experiments will be presented. Adsorption isotherms give the vapor pressure depending on the coverage of gas on the surface. Isotherms of $H_2$ at 4.2K and of CO and $CH_4$ at 77K have been measured.

Thermal Desorption Spectroscopy, that allow to determine the average binding energy between the gas and the surface, have been carried out for the four gases, for different initial coverages.

It has been measured that amorphous carbon is a porous material which can store more gas at cryogenic temperature than usual technical surfaces such as copper or stainless steel. The consequences for the accelerator will be discussed. A model to compute the pressure rise in the vacuum pipe, depending on the temperature variation and on the initial coverage, is under development.

3:00pm **VT-ThA3 Heavy ion-induced Desorption and its Impact on Next Generation Accelerators**, ***Markus Bender***, *H. Kollmus,* GSI Helmholtzzentrum für Schwerionenforschung GmbH, Germany, *E. Mahner*, CERN, Switzerland **INVITED**

Dynamic pressure increases in vacuum systems of particle accelerators have been observed since almost 50 years. Since the turn of the millennium, the dynamic vacuum turned out to be an intensity limitation in particle accelerators, e.g. in the Low Energy Antiproton Ring (LEAR) at CERN or the heavy ion synchrotron SIS18 at GSI. Here, charge exchanged lost beam ions stimulate the release of gas from the chamber walls and the subsequent pressure increase leads to increased beam-loss. Hence the effect is self-amplifying and can lead to severe deterioration of the vacuum to the point of complete beam-loss. Consequently heavy ion-induced desorption is an issue for next-generation heavy ion accelerators such as the FAIR facility or Spiral2 with highest beam intensities.

To come up against this dynamic vacuum effect, several measures have been conducted. In particular the physics behind the ion-induced release of gas was investigated. For that purpose, several samples have been irradiated with ion beams of different parameters and the resulting desorption yields have been measured. A broad range from some 10 to several 10,000 released gas molecules per incident ion was observed. From the gathered results a clear picture of the underlying process of ion-induced desorption was drawn. It could be shown that the desorbed gas is originating mainly from the surface or surface-close regions of the target. But in contrast to earlier ideas, sputtering of the oxide layer on metals was not identified as the source for the desorbed gas. Latest experiments prove that pre-treatment of critical components is most important to minimize the desorption yield and therefore, especially thermal annealing was investigated in detail.

Besides experimental findings a model calculation was developed that is able to describe and compare desorption yields of different collision systems. The calculation is based on the inelastic thermal spike model and describes ion-induced desorption as enhanced thermal desorption due to a transient overheated spot around the ion impact.

Presently we are able to propose materials, coatings, and treatment procedures for best performance in particle accelerator vacuum systems.

4:00pm **VT-ThA6 Outgassing Behavior of Different Oxide Ceramic Materials**, ***Katharina Battes***, *C. Day, V. Hauer,* Karlsruhe Institute of Technology (KIT), Germany

In general, ceramics show interesting mechanical, thermal and electrical properties and are supposed to have relatively low outgassing rates. Therefore, in vacuum applications they are often used for feedthroughs for example. However, quantitative numbers on outgassing of most of the ceramic materials are hard to find in literature.

For this reason the outgassing of different ceramic materials was studied at the Outgassing Measurement Apparatus (OMA), which uses the difference method. First, oxide ceramics like alumina, magnesia, silica, and MACOR®, which consists of silica and other oxide ceramics, were measured. All measurements were performed at room temperature, 100 °C and 200 °C to investigate the temperature behavior of outgassing. Additionally, the outgassing species were determined by a quadrupole mass spectrometer.

The paper shows quite low outgassing rates for most of the examined ceramics. After 100 h at room temperature an outgassing rate of about $2\cdot10^{-8}$ $(Pa\cdot m^3)/(s\cdot m^2)$ is achieved for alumina for example. The mass spectra show similar residual gas spectra as seen for metals. Thus, these materials can be used in ultra-high vacuum applications.

4:40pm **VT-ThA8 APS-Upgrade Storage Ring Vacuum System Sector Mockup and Vacuum R&D Activities**, ***Jason Carter***, Argonne National Laboratory

As the APS Upgrade project continues in its preliminary design phase the APS-U storage ring vacuum system plans continue to mature while ongoing R&D activities and analysis are validating and strengthening the design. The storage ring magnets and structural support designs constrain the system to have narrow aperture vacuum chamber dimensions and limit allowable UHV pumping elements and locations. Monte-Carlo vacuum system analysis has indicated that the pressures and performance should meet requirements during and after accelerator commissioning. The margin of error for analysis must be better understood so a number of ongoing R&D efforts are helping to better predict and improve the performance.

A 28 meter length full sector vacuum system mockup will be installed in Fall 2017 and will include prototype vacuum chambers and all pumping elements. A sector mockup vacuum test plan will be presented which examines pumping speeds, outgassing rates, and the pumping conductance. NEG coating performance will be key to APS-U vacuum success and prototypes and further analysis are helping evaluate current coating plans and the option of adding more coatings. Finally, R&D proposals are progressing to measure photon stimulated desorption from APS-U style chamber designs.

5:00pm **VT-ThA9 Numerical Tools for Particle Accelerator Vacuum Systems**, ***Giulia Lanza***, SLAC National Accelerator Laboratory

A number of different gas density simulation programs have been applied in the design of the SLAC National Accelerator Laboratory's LCLS-II accelerator's vacuum system. Starting from these basic programs, this talk gives an overview of the available numerical methods for the analysis and design of a linear accelerator vacuum system.

Programs like Pressure5, LTspice, Vaccalc, Molflow+ and others are described and compared. Their optimal domain of applicability, the pros and cons are discussed.

5:20pm **VT-ThA10 Developing Particle Control Infrastructure for the ESS High Beta Project at STFC Daresbury Laboratory**, ***Mark Pendleton***, STFC Daresbury Laboratory, UK

As part of a UK In-Kind contribution to the European Spallation Source (ESS), STFC-Daresbury laboratory has agreed to procure, fabricate, test and deliver 84 + 4(5-cell) high-beta superconducting 704.41 MHz dressed cavities according to ESS requirements.

As part of the test phase and re-work at STFC the cavities will have to be processed and connected in a particulate controlled environment.

This paper will describe the developments of the Main Cleanroom facility which will be utilised for the workflow of the High Beta Cavity to undertake a High Pressure rinse cycle. It will also cover the Cryostat Insert stands and the design of the Modular cleanroom solutions that will be utilised to connect the cavity under ISO 4 conditions to the new Vertical Test Cryostat Insert developed at STFC.

5:40pm **VT-ThA11 Functional Coatings for Gauges and Components**, *B. Andreaus, C. Strietzel,* ***Martin Wüest***, INFICON Ltd., Liechtenstein, *C. Guerra-Nuñez, M. Ruoho, I. Utke, J. Michler, X. Mäder, M. Polyakov*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Process industry is constantly changing. New manufacturing processes using new chemistries are developed. Yet, quality and cost pressure demand that processes are highly reliable, repeatable and need fewer maintenance interruptions. For vacuum sensors this means that they need to have a longer life in process before they need to be exchanged due to sensor degradation caused by process corrosion. To cope with this, we have investigated ways to protect the vacuum sensors from process related influences. Coatings are a good way to protect a surface from corrosion while leaving the underlying structural part without change. Coatings can be adapted to the changing customer needs. We will present results from experiments we have done with gauges and components using different protective layers.

6:00pm **VT-ThA12 60 Years of Ion Pumps: From the Invention to the Latest Developments**, ***Mauro Audi***, Agilent Technologies, Italy

Since their invention in 1957 at Varian Associates as a pumping device for electron tubes at relatively high pressures , Ion Pumps have continuously moved towards lower pressures , and nowadays they are the pumps of choice for most of UHV applications in both research and industrial field

This includes a large a variety of high and ultra high vacuum systems , from Particle Accelerators to Synchrotron Light Sources and Gravitational Wave Detectors , from Scanning Electron Microscope to Surface Analysis and Medical Equipment

Application requirements have changed dramatically in these 60 years in terms of starting and operating pressures , pumping performances , ability of pressure reading , cleanliness , particle emissions , safety , resistance to radiation .

The latest developments on Ion Pump Technology are presented , including :

- a new combination of magnetic field and cell dimensions to realize the first ion pump with the maximum pumping speed in the low pressure range

- a new vacuum firing process to minimize the outgassing and reduce particles

- an anode design that minimizes the field emission and the leakage current , and additional shields that minimize charged particle emissions

-a controller design that allows starting Ion Pumps with a very limited power and can vary voltage supplied to the ion pump in order to optimize both the pumping performances and the pressure reading ,

- a combination of ion pumps with NEG pumps in order to reach the lowest ultimate pressure

## 2D Materials Focus Topic
## Room: Central Hall - Session 2D-ThP

## 2D Materials Poster Session

**2D-ThP1 In-situ Analysis of Electronic Structure of monolayer $MoS_2$ using Photoemission Spectroscopy and Kelvin probe**, ***JaeGwan Chung***, *U.J. Kim, D. Yun, Y.S. Kim, J. Shin*, Samsung Electronics, Republic of Korea

Although two-dimensional monolayer transition metal dichalcogenides reveal numerous unique features that are inaccessible in bulk materials, their intrinsic properties are often obscured by environmental effects. Among them, work function, which is the energy required to extract an electron from a material to vacuum, is one critical parameter in electronic/optoelectronic devices.

In this study, we systematically measure the electronic structure of monolayered $MoS_2$ – work function, energy band gap, conduction band and valence band structure by in-situ photoemission spectroscopy (PES), inverse photoemission spectroscopy (IPES), reflective electron energy loss spectroscopy (REELS) and Kelvin Probe (KP) under various ambient condition (air, ultra-high vacuum, oxygen and nitrogen gases). The energy band gap by REELS of monolayer $MoS_2$ on $SiO_2$ is 1.7 eV. It shows a increase as compared with the optical band gap of 1.2 eV of Bulk $MoS_2$ [1]. And also, the valence band offset and conduction band offset of mono layer $MoS_2$ are shifted higher binding energy side of 0.5 eV. A work function measured by in-situ KP of 4.04 eV in vacuum was converted to 4.47 eV with $O_2$ exposure, which is comparable with a large variation in graphene.

The homojunction diode by partially passivating a transistor reveals an ideal junction with an ideality factor of almost one and perfect electrical reversibility. The estimated depletion width obtained from photocurrent mapping was ~200 nm, which is much narrower than bulk semiconductors.

References

[1] Y. Zhang, Nature nanotech. **9** 111 (2014).

**2D-ThP2 Reliable Passivation of Black Phosphorus by Thin Hybrid Coating**, *S. Gamage*, ***Alireza Fali***, *N. Aghamiri*, Georgia State University, *L. Yang, P.D. Ye*, Purdue University, *Y. Abate*, Georgia State University

**Topic:**2D materials

Black phosphorus (BP) possesses several extraordinary properties such as layered structure but with a unique puckered single-layer geometry, thickness dependent direct bandgap, high carrier mobility and anisotropic in-plane properties that not shared by other exfoliable materials that are highly desirable from the point of view of fundamental science and modern optoelectronics applications. The excitement about this material has always been accompanied by unreserved skepticism due to its extraordinary degradation under ambient conditions. Here we show ambient degradation of exfoliated BP can be effectively suppressed using thin layer of hybrid MOCVD coating of BN followed by ALD coating of Al2O3. We have extensively studied the time dependent surface, optical and electrical properties of BP encapsulated by BN and/or Al2O3 using nanoscale infrared imaging and I-V characterizations. Our results show hybrid thin layer (~5 nm) BN/Al2O2 coated BP exfoliated on SiO2 substrate is protected from degradation in ambient for over 45 days much longer than those coated on BN or Al2O3 layers only as well as those exfoliated on Si substrate. Our theoretical modeling of the experimental degradation growth pattern shows that the influence of neighboring elements on the degradation of a given element is minimal for BP flakes with hybrid coating. Electrical characterization further confirms the effectiveness of BN/Al2O3 as encapsulation layer and gate dielectrics with minor changes after several weeks.

**2D-ThP3 Temperature-dependent Photo-current Behaviors of CVD-grown $MoS_2$ layers**, ***Soyeong Kwon***, *E. Kim, Y. Cho*, Ewha Womans University, Republic of Korea, *Y. Kim, B. Cho, D.-H. Kim,* Korea Institute of Materials Science, *D.-W. Kim*, Ewha Womans University, Republic of Korea

$MoS_2$, a representative 2D atomically thin semiconductor, has unique optical, electrical, and mechanical properties. There have been intensive research efforts to fabricate $MoS_2$-based optoelectronic devices due to its sizable band gap (1.2 ~ 1.8 eV). In this work, we investigated transport behaviors of $MoS_2$ layers, grown by chemical vapor deposition (CVD), in dark and under illumination of visible light [1,2]. CVD techniques can produce high-quality, large-area $MoS_2$ thin films with a high throughput. Surface potential maps near the electrode/$MoS_2$ contacts were obtained using Kelvin probe force microscopy, which clearly showed how the potential gradient near the contacts could affect the collection of the photo-generated carriers. The dark- and photo-current behaviors of the devices in dark and light were measured while varying the sample temperature (100 ~ 300 K). The temperature dependent current-voltage characteristics helped us to understand the carrier transport mechanism and its roles in the photo-detection of the CVD-grown $MoS_2$ thin films.

1. Y. Cho et al., *ACS Appl. Mater. Interfaces***8**, 21612 (2016).

2. Y. Cho et al., *ACS Appl. Mater. Interfaces***9**, 6314 (2017).

**2D-ThP4 Controlling Charge Density Wave Transition in Monolayer $TiSe_2$**, ***Sadhu Kolekar***, *M. Batzill*, University of South Florida

Layered transition metal dichalcogenides (TMDCs) have been studied for their charge density wave (CDW) and superconductivity transitions. $TiSe_2$ is interesting because traditional explanations for CDW formation based on electron phonon coupling described by Fermi surface nesting does not apply. Instead an unconventional excitonic mechanism has been invoked. The well-established dependence of the exciton binding energy on the number of layers in TMDCs implies that the CDW transition in $TiSe_2$ should also be layer dependent. Furthermore, the dielectric properties of the substrate for monolayer $TiSe_2$ should exert further control over the excitonic properties and thus the CDW transitions in $TiSe_2$. Here we investigate mono- to few-layer $TiSe_2$ films grown by molecular beam epitaxy on HOPG or $MoS_2$ substrate by variable temperature scanning tunneling spectroscopy. We show that the band gap opening and CDW transition temperature in monolayer is strongly increased compared to bulk $TiSe_2$ and correlates with the expected exciton binding energy dependence. Interestingly, we also observe phase coherence peaks in monolayer $TiSe_2$. The phase coherence occurs, however, at a much lower temperature than the CDW transition, suggesting that formation of an excitonic condensate is possible but is not essential for CDW formation.

**2D-ThP5 Growth and Characterization of $MoTe_2$ on GaTe by Molecular Beam Epitaxy**, ***Paula Mariel Coelho***, *M. Batzill*, University of South Florida

$MoTe_2$ exist in semiconducting (2H) and metallic (1T') polymorphs. The potential for switching between these phases makes it a promising 2D material for phase change applications. In this study we are investigating van der Waals epitaxy of single layer $MoTe_2$ on different substrates and growth conditions. Specifically, we aim at selectively growing 2H or 1T' phases by molecular beam epitaxy. Using van der Waals substrates with symmetries similar to the 2H or 1T' phases of $MoTe_2$ we are aiming at obtaining epitaxial single crystalline monolayer materials. Specifically, we propose GaTe to be a suitable substrate for the growth of 1T'-$MoTe_2$. We characterize the substrates and $MoTe_2$-films *in-situ* by scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS) and angle resolved photoemission spectroscopy (ARPES). Furthermore the thermal stability and phase change behavior of these monolayers are investigated.

**2D-ThP7 Single Layer $VSe_2$: A Ferromagnetic 2D Material**, ***Manuel Bonilla***, *S. Kolekar, H. Coy Diaz, Y. Ma, M. Batzill*, University of South Florida

$VSe_2$ has been proposed to be ferromagnetic in single- to few- layer form. However, the high reactivity of $VSe_2$ makes mechanical exfoliation to single layers and subsequent magnetic characterization challenging. Here we grow $VSe_2$ by molecular beam epitaxy in ultra-high vacuum. We characterize the film-growth and materials properties *in-situ* by scanning tunneling microscopy/spectroscopy and photoemission spectroscopy. High quality single- to few- layer materials are obtained, with the well-known charge density wave transition for bulk $VSe_2$ persisting to monolayer material. For magnetic characterizations we protect the single- to few- layer materials from oxidation by a few nanometer thick selenium capping layer. We observe a strong ferromagnetism for the single layer, which decreases with number of layers. This study shows that VSe2 single layer is indeed a promising 2D ferromagnetic material, whose magnetic properties can be tuned by the layer thickness.

**2D-ThP8 Surface Functionalization of Few-layer $MoS_2$ for Atomic Layer Deposition using Gold Chloride Salts**, ***Jaron Kropp***, UMBC, *T. Gougousi*, University of Maryland, Baltimore County

Transition metal dichalcogenides such as $MoS_2$ have attracted much interest in the field of nanoelectronics in recent years. $MoS_2$ is a layered material with a hexagonal structure similar to graphene. Unlike graphene, however, $MoS_2$ is a semiconducting material with an indirect band gap of ~1.2 eV in bulk form and a direct band gap of ~1.8 eV in monolayer form. As such, $MoS_2$ has attracted interest as a possible channel material in field-effect transistors. An important feature of the modern field-effect transistor is the gate dielectric. In the past decade, the electronics industry has transitioned from using native silicon oxide as the gate dielectric to using high-k metal oxides deposited via atomic layer deposition. Field-effect devices fabricated from $MoS_2$ will thus require the growth of metal oxides on the $MoS_2$ surface. Unfortunately, the sulfur-terminated $MoS_2$ surface is hydrophobic and not conducive to metal oxide film growth using atomic layer deposition. As such, the surface must be functionalized prior to deposition. Here, we report a novel wet chemistry method for functionalization of $MoS_2$ surfaces using gold chloride salts.

Mechanically exfoliated $MoS_2$ surfaces are treated by immersion in a solution of $HAuCl_4$ or $AuCl_3$ for 5-60 seconds and are subsequently subjected to atomic layer deposition of $Al_2O_3$ using trimethylaluminum and water as precursors. We measure the effectiveness of the surface treatment by investigating the post-deposition surface topography using atomic force microscopy. Our hypothesis is that immersion of the $MoS_2$ surfaces in the gold chloride solution will leave behind adsorbed gold chloride molecules which render the surface hydrophilic and amenable to the growth of metal oxide films. While untreated surfaces show island growth, gold chloride-treated surfaces show more coalesced films. Treatment for at least 30 seconds results in a reduction of the film RMS roughness by a factor of 4 compared to untreated surfaces after deposition of 3 nm (nominal thickness) $Al_2O_3$ at 200°C. Film surface coverage improves from 50-60% on untreated surfaces to 80-99% on surfaces treated for 10 seconds and finally to complete film coverage on surfaces treated for 30 and 60 seconds. Surface roughness and coverage is investigated as a function of film thickness and deposition temperature, and provides information on initial growth mechanisms and process conditions for the growth of conformal, high-quality films.

**2D-ThP10 Alternative Pathway to Silicene Synthesis via Surface Relaxation of Hexagonal-$MoSi_2$ Crystallites**, ***Cameron Volders***, *E. Monazami, G. Ramalingam, P. Reinke*, University of Virginia

The 2D material community has been dominated by Graphene, however, more recently, different single layer materials have garnered more attention including transition metal dichalcogenides (TMDs), silicene, and germanene. Silicene is particularly intriguing due to its potential for integration into silicon based devices. The most frequently used method for synthesizing silicene has been the deposition of monolayer (ML) amounts of Si onto Ag (111). The resulting layer(s) exhibit a honeycomb symmetry, which have been identified as silicene. An alternative interpretation of the Si-Ag system suggests the formation of 2D Ag-Si surface alloy rather than the formation of a well-defined silicene layer.

Our work will present an approach, which offers an alternative pathway for growing silicene layers, based on the observation of a Silicene-like reconstruction (SLR) on the surface of hexagonal-$MoSi_2$ crystallites. Scanning Tunneling Microscopy and Spectroscopy were the primary techniques used for this study. H-$MoSi_2$ crystallites are grown by depositing Mo onto a Si (001) surface followed by annealing. These crystallites are terminated by the (0001) plane which is comprised of Si hexagons with a Mo atom residing in the center. Upon annealing, the Si atoms decouple from the underlying h-$MoSi_2$ crystallites and a honeycomb pattern with the lateral dimensions of a low-buckled silicene structure is observed.

We first discuss the optimal parameter space where the SLR is consistently reproduced. This regime includes depositing 2-5 MLs of Mo onto a Si (001) substrate and annealing around 650 - 800˚C. In this regime the SLR structure is readily observed and the geometrical parameters are nearly identical to that of a (√3X√3) silicene superstructure. Additional features of the SLR such as a well-defined 'rim' structure and defect motif will also be discussed.

The area of the SLR structure is controlled by the surface area of the h-$MoSi_2$ crystallites, therefore, the second portion of this work will discuss how to control the size and distribution of these crystallites, thus the area of the SLR layer. This becomes critical for future device integration and assessing the detailed bonding structure with AR-UPS.

We would like to thank the Office of Naval Research for supporting this work.

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**2D-ThP11 CVD Grown 2D Metal Carbides using Folded Cu/Metal Foils**, ***Kwonjae Yoo***, *I.S. Kang, G. Kim, M.S. Hyun, Y.C. Park,* National Nanofab Center (KAIST), Republic of Korea, *S. Lee, C. Hwang*, Korea Research Institute of Standards and Science, Republic of Korea

Two dimensional (2D) metal carbides (MC) are recently entered in a playground of 2D materials world. Unlike conventional 2D materials, such as graphene and transition metal chalcogenides, they has shown the unique properties of 2D metallic- and superconducting- state. Moreover, their high thermal and chemical stability due to covalent-ionic bonding between metal and carbide atoms can offer a great advantage for harsh environmental sensor applications.

2D MC are obtained by selective extraction method from ternary carbides or by recently chemical vapor deposition (CVD). While monolayer metal carbides known as MXenes which produced by selective extraction method have shown defects and surface terminations which affect their physical properties, CVD grown monolayer metal carbides such as Mo2C, W2C are known to have very low defects [1, 2]. This modified CVD method uses Cu foil on molybdenum foil with melted Cu and moly alloy surface near the temperature of the Cu melting point.

Here we present the CVD using Cu foil inside folded Mo foil for growing metal carbides. The folded Mo foil inside CVD quartz tube not only prevents from evaporation of melted Cu, but also provides uniform gas flow. These growth condition seem to be positive effect on the growth of large area and uniform monolayer metal carbides such as Mo2C and W2C. We investigated CVD grown monolayer Mo2C using electron back scattering diffraction (EDSD), tunneling electron microscopy (TEM), and low temperature electron transport. Growth results depending on Cu crystallographic orientation will be discussed.

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**2D-ThP12 Scanning Tunneling Microscopy and Spectroscopy of Wet Chemically Synthesized Porous Graphene Nanoribbons**, ***Kaitlyn Parsons***, *A. Radocea*, University of Illinois at Urbana-Champaign, *M. Pour*, University of Nebraska - Lincoln, *T. Sun, N. Aluru*, University of Illinois at Urbana-Champaign, *A. Sinitskii*, University of Nebraska - Lincoln, *J.W. Lyding*, University of Illinois at Urbana-Champaign

The bottom-up wet chemical synthesis of graphene nanoribbons (GNRs) opens interesting opportunities for tailoring the GNR structure with atomic precision [1]. Atomically precise porous GNRs are a new chemically synthesized variation for which the fabrication procedure yielding multiple pores in a single ribbon and the electronic details of the ribbon have not been reported. In this work, porous GNRs are dry contact transferred in ultrahigh vacuum to clean silicon and III-V semiconducting substrates and examined using UHV scanning tunneling microscopy (STM) and spectroscopy (STS). STM imaging confirms the expected porous structure and indicates a unique electronic feature at the graphene nanopores, and STS measurements indicate a 2.0 eV bandgap. These results are compared to first-principles DFT simulations in which an increased local density of states at the pores is predicted. A GW correction predicts a 3.24 eV bandgap. Illumination of pore effects in GNRs contributes to an increased understanding of the tunability of GNR electronic structure. Porous GNRs have potential applications in molecular filtration, detection and DNA sequencing.

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**2D-ThP13 Surfactant-Exfoliated 2D Molybdenum Disulphide (2D-$MoS_2$): The Role of Surfactant upon the Hydrogen Evolution Reaction**, ***Simon Hutton***, Kratos Analytical Limited, UK, *S.J. Rowley-Neale, C.E. Banks*, Manchester Metropolitan University, UK, *C.J. Blomfield, S.J. Coultas, A.J. Roberts, J.D.P. Counsell*, Kratos Analytical Limited, UK

Hydrogen, produced via the electrolysis of water, is a promising alternative to fossil fuels. Hydrogen may be transported in bulk from areas of energy production to areas of energy consumption and used to generate electricity directly in fuel cells. One of the major problems limiting the widespread take-up of hydrogen based technology is the high cost of platinum which is used as a catalytic electrode material in both water electrolysis and fuel cells.[1]

Recent research has focused on finding a more cost effective electrode materials to catalyse the Hydrogen Evolution Reaction (HER). Studies have shown that 2D Molybdenum disulphide (2D-$MoS_2$) can be used as an effective electrocatalyst towards the HER.[2] Surfactant (e.g. sodium cholate, SC) mediated aqueous liquid phase exfoliation is a common method of fabricating 2D-$MoS_2$ nanosheets. This method produces defect free flakes with nanometer lateral size (2D-$MoS_2$-SC).

This study investigates the effect of using sodium cholate to produce the 2D nanosheets (2D-$MoS_2$-SC) on the electrocatalytic behaviour towards the HER when compared to 2D-$MoS_2$ produced without a surfactant. The 2D-$MoS_2$-SC nanosheet surface was characterised using X-ray photoelectron spectroscopy. Electrocatalytic performance was evaluated by measuring the HER onset potentials, current densities and Tafel values.

**2D-ThP14 Low Damage Layer-controlled Thinning of Black Phosphorus by a Low Energy Ar$^+$ Ion Beam**, ***Jinwoo Park***, *D.S. Kim, W.O. Lee, M.K. Mun, K.S. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Black phosphorus (BP) is one of the most interested two-dimensional (2D) layered materials due to their unique properties of energy band gap change from 0.3 eV (bulk) to 2.0 eV (monolayer) depending on the number of BP layers for the application of nanoeletronic devices. Currently, for the fabrication of 2D BP materials, a thinning technique from bulk material to 2D material needs to be used while controlling the removed layer thickness. In this study, low-damage layer thinning of BP was performed by using an Ar$^+$ ion beam method and its BP thinning characteristics were investigated. By using the Ar$^+$ ion energy of ~ 45 eV, the BP could be thinned with the thinning rate of ~ 5 Å/min down to bilayer without increasing the surface roughness and changing the chemical binding states. Back-gate BP field-effect transistors (FETs) fabricated with a BP thinned to bilayer ~ 10 layers by the Ar$^+$ ion beam exhibited the electrical characteristics similar to those of pristine BP FETs such as a high-drain current and 7000 on/off ratio suggesting no electrical damage on the BP layers thinned by the low-energy Ar$^+$ ion beam. Therefore, it is believed that the low energy Ar$^+$ ion beam technique used in this study can precisely control thickness 2D materials like BP without any damages and can be a promising thinning method for fabricating 2D-based devices.

**2D-ThP15 Controlled Growth of Multilayered Hexagonal Boron Nitride on Ni-Cu Alloys**, ***Karthik Sridhara***, Texas A&M University, *B.N. Feigelson, J.K. Hite*, US Naval Research Laboratory, *L.O. Nyakiti*, Texas A&M University Galveston

Hexagonal boron nitride (h-BN) has been frequently studied as a potential substrate and a tunnel dielectric for two-dimensional materials such as graphene and transition metal dichalcogenides. Large area (>1 cm$^2$) single and multilayered h-BN films have been successfully grown using chemical vapor deposition (CVD) on various single crystal and polycrystalline transition metal substrates such as Cu, Ni, Pt, and Ag. Of these substrates, polycrystalline Cu followed by polycrystalline Ni are by far the most commonly used substrates for CVD growth. Despite the popularity of polycrystalline Cu and Ni for the growth of h-BN, controlled uniform growth of multilayered (>3 layers) and few-layered (<3 layers) h-BN still remains a challenge.

We propose a method to grow few and multilayered h-BN on nickel-copper (NiCu) alloys, and control the thickness of h-BN by varying the concentration of Cu in NiCu alloy samples. These NiCu alloys are prepared by electroplating Cu onto high purity (99.8%) Ni foils (25 µm) and thermally annealing them at 1030°C for > 3 hours in $H_2$ environment. The Cu concentration in the alloy can be controlled by the electroplating current density and time to give desired weight percent of Cu deposited on Ni foils. NiCu alloys with four different Cu weight percentages (10%, 20%, 30%, 40%) are prepared using electroplating and thermal annealing procedure. The alloyed foils are subsequently cut into smaller pieces (~1 cm$^2$) and are further annealed before h-BN growth. h-BN films are grown on these alloyed samples at 1030°C using borazane as the precursor, with $H_2$ and $N_2$ as the carrier gases, and high purity Cu (99.98%) and Ni (99.8%) are used as control samples. We use energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) to quantify the Ni and Cu concentration in the alloy. Scanning electron microscopy (SEM) is used to assess the surface morphology of the alloys, and ascertain the crystal size of h-BN films. We use Fourier transform grazing-incidence infrared reflection absorption spectroscopy (FT-IRRAS) to assess the h-BN film growth. Our preliminary results show that there is an immediate increase in the amount (thickness) of h-BN with the introduction of Cu in the NiCu alloy. We observe a subsequent decrease of h-BN thereafter with increasing Cu concentration in the NiCu alloy samples. We consistently observe that the thickest h-BN films, as calculated by FT-IRRAS peak area, grow on $Ni_{90}Cu_{10}$ while the thinnest grow on $Ni_{60}Cu_{40}$. We also observe that the alloy grain size decreases with increasing Cu concentration. The role of alloy surface morphology and the h-BN growth kinetics will also be discussed.

**2D-ThP16 Metal Oxide/Functionalized Graphene Oxide Composite as Highly Stable Lithium Ion Battery Anode with Enhanced Performance**, ***SunSook Lee***, Korea Research Institute of Chemical Technology(KRICT), Republic of Korea, *S. Ji, J.Y. Ju, S-K. Kim, J.K. Kim, S. Choi*, Korea Research Institute of Chemical Technology(KRICT)

Metal-oxide based lithium ion battery(LIB) anodes theoretically should provide high specific capacity, but their disappointing experimentally measured capacity and cycle stability inhibit their commercial usage. Here, we propose a simple method to process Metal oxide/functionalized-graphene-oxide(fGO) composite anode, in which fGO is inserted as the current path that simultaneously enhances the specific capacity to reach near the theoretical capacity and the cyclic stability at least up to 200 cycles for the metal oxide based anodes.

**2D-ThP18 Exploration of Hybrid 2DEG/Ferroelectric Heterostructure Fabrication Methodology**, ***Stephan Young***, *E.J. Moon, R. Doucette, A.N. Caruso*, University of Missouri - Kansas City

The hybrid two-dimension electron gas (2DEG)/ferroelectric (FE) heterostructure system has many promising applications, including field effect transistors and non-volatile memory. Such devices exploit the ambipolar field effect, utilizing the high local electric field produced by the FE substrate to shift the Fermi level in the 2DEG. Thus, controlling magnitude and direction of polarization of the FE can significantly alter conductivity and majority charge carrier in the 2DEG. FE/2DEG hybrid devices are typically fabricated by transferring the 2DEG onto the FE substrate. However, this process often introduces adsorbates onto the surface of the 2DEG and FE, resulting in a poor interface and degrading the electric field at the 2DEG. This problem can be partially mitigated by improving the transfer process, but direct growth is a path to eliminate the problem entirely. This work explores the effect of different transfer processes in comparison to chemical vapor deposition growth of 2DEG's directly on FE substrates. The study aims to elucidate the interfacial interaction between 2DEG's (i.e. transition metal dichalcogenides and graphene) and low-coercivity, high-remnant-polarization perovskite ferroelectrics. Characterization of the 2DEG domain size was completed with atomic force microscopy, the number of layers confirmed with Raman spectroscopy, and the conductivity of each growth was measured.

This work was supported by the Office of Naval Research (ONR) under N00014-16-1-2067.

**2D-ThP20 Effect of Stacking Orientation and Sag on the Strength and Fracture of Graphene Oxide**, ***Teng Cui***, *C.H. Cao, S. Parambath Mundayodan, Y. Sun, T. Filleter*, University of Toronto, Canada

One great challenge in translating the extraordinary mechanical properties of isolated 2D materials to impact real applications is to understand, and bridge the gap, between monolayer and multilayer properties. Bilayer films, as the most fundamental step towards this challenge, require systematic study to unveil the interaction between layers and elucidate the effect on mechanical behavior. Here, bilayer graphene oxide (GO) with different crystalline stacking orientation and sag conditions will be presented, and the resulting effect on the material strength and fracture will be discussed in detail.

Highly oxidized bilayer GO films were prepared on perforated substrates by a solution-based method, from which different interlayer crystalline stacking angle and sagging depth were obtained and characterized. Atomic force microscopy-based mechanical testing revealed higher strength of aligned (small stacking angle) bilayers as compared to misaligned (large stacking angle) counterparts. Further transmission electron microscopy analysis of fracture surface revealed through-film fracture for the aligned case and individual layer cracking for the misaligned case, casting light on the origin of the strength discrepancy. In addition, the suspended GO films present different sagging depth, which in turn is found to effect the load carrying capacity and the fracture behavior significantly. Our results demonstrated that bilayer GO with ~165 nm sag doubles the fracture force as compared to ~ 40 nm sag. A deeper understanding of the configurational effect, e.g., stacking orientation and sagging, on the mechanical behavior will better facilitate engineering GO for various applications at different size scales.

**2D-ThP22 Single Atom Manipulation and Controllable Atom by Atom Assembly in 2D Materials via Scanning Transmission Electron Microscopy**, ***Sergei Kalinin***, *O. Dyck, S. Kim, S. Jesse*, Oak Ridge National Laboratory

Fabrication of structure atom-by-atom has remained one of the longest-held dreams of nanoscience, as a key element of nanotechnology and penultimate step for understanding physics and chemistry on the atomic level. The development of scanning tunneling microscopy (STM) in the early 1980s has demonstrated the potential of an atomically sharp tip to induce atomic motion on a surface, originally perceived to be detrimental to microscope operation. The work by Eigler at IBM in the early 1980s demonstrated that tip induced atomic motion can be used for the assembly of functional atomic structures, an accomplishment believed to be one of the key factors that lead to the nanotechnology revolution of the last decades. However, STM operation necessitates low temperature ultra-high vacuum environments and typically results in structures confined to reactive surfaces. Correspondingly, it took over 20 years to transition from atomic manipulation by STM to viable pathways for single-atom devices. This in turn, necessitates the search for alternative methods for single atom manipulation and atom-by-atom assembly.

Here we demonstrate that the sub-atomically focused beam of a scanning transmission electron microscope (STEM) can be used to controllably manipulate individual dopant atoms in a 2D graphene lattice. We demonstrate the manipulation of adsorbed source materials and the graphene lattice with the electron beam such that individual vacancy defects can be controllably passivated by Si substitutional atoms. We further demonstrate that these Si defects may be directed through the lattice via e-beam control or modified to form new defects which can incorporate new atoms into the graphene lattice. We further explore the application of beam to probe local dynamics within individual or between adjacent atomic sites. These studies demonstrate the potential of STEM for atom-by-atom nanofabrication and fundamental studies of chemical reactions in 2D materials on the atomic level.

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## Applied Surface Science Division
## Room: Central Hall - Session AS-ThP

## Applied Surface Science Poster Session

### AS-ThP1 Depth Profiling Adventures in the Non-Semiconductor Chemical Industry, *Kathryn Lloyd*, *J.R. Marsh*, DuPont

Until recently, technology development for SIMS depth profiling was centered around flat semiconductor wafers. Sputter rates could be determined using standards and doped standards. Experimental protocols continue to be optimized, but figures of merit are for the most part understood.

With the expansion of computer memory and disk space, sophisticated vendor and third-party software, and new cluster beam sputter sources, SIMS (specifically ToF-SIMS) depth profiling is now being applied to distinctly non-flat, standards-defying, or just structurally-complex systems. In the realm of inorganic depth profiling, the quasi-parallel spectral acquisition compared to quadrupole mass analyzers and the use of multivariate statistics can mitigate many problematic mass interferences. For organic/polymeric systems such as fibers, resins, and coatings, huge Argon gas cluster sputtering enables molecular detection of sub-surface species. Hybrid systems such as OLEDs and paints continue to present challenges because of the different sputtering conditions needed for the different layers. For all of these samples, the ability to visualize the depth profiling data in 3D graphics is very powerful.

One could argue that these experiments are less true "depth profiling" experiments and more "just sputtering" to obtain sub-surface chemical information. In any case, this presentation will show examples of sputtering ToF-SIMS applications in an industrial environment that have been made possible through the implementation of new Argon cluster sputter beams and/or the use of multivariate statistics.

### AS-ThP2 High-energy Cluster Ions - Minimising Depth Profiling Artifacts for Solid-state Electrolytes, *J.D.P. Counsell*, Kratos Analytical Limited, UK, ***Chris Moffitt***, Kratos Analytical Ltd, *A.J. Pearse*, University of Maryland, College Park, *C.J. Blomfield*, *S.J. Coultas*, Kratos Analytical Limited, UK, *G. Rubloff*, University of Maryland, College Park

Classical lithium ion batteries rely on a liquid electrolyte however there have been significant developments towards replacing liquid electrolytes with solid state thin-films. Thin-film lithium ion batteries offer improved performance by having a higher average output voltage, lighter weights thus higher energy density, and longer cycling life than typical liquid electrolyte batteries [1]. In order to construct a thin film battery it is necessary to fabricate all the battery components, such as an anode, a solid electrolyte, a cathode and current leads into a multi-layered thin film. Lithium phosphorous oxynitride (LiPON) is widely used as the electrolyte in solid state micro-batteries due to low electronic conductivity, increased durability to cycling and ease of preparation.

Here we will use convention surface analysis techniques of XPS and sputter depth profiling to understand the surface and bulk chemistry of LiPON thin films formed via atomic-layer deposition (ALD) [2]. XPS yields quantitative information regarding the elemental composition of the near surface region to a depth of <10 nm. The elemental composition as a function of depth is probed and comparisons are made between conventional monatomic depth profiling and cluster depth profiling. We will also analyse complete battery stacks in their virgin and cycled states and discuss changes in elemental distributions at the interfaces between the electrodes and the solid electrolyte.

We demonstrate that the use of monatomic Ar ions is unsuitable for profiling materials with mobile light elements (Li) as the build-up of positive charge causes migration leading to erroneous depth composition. An alternative is proposed whereby the analyst uses 20 kV high-energy cluster ions in an attempt to mitigate the effects of ion migration and thereby improving confidence in the validity of the results.

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### AS-ThP3 The Internal Composition and Structure of Fish Scales Investigated by ESCA and SEM, ***Gerry Hammer***, *S. Murcia*, *E. Lavoie*, *L.J. Gamble*, *D. Arola*, *D.G. Castner*, University of Washington

Fish scales are one example of a biological structure that provides physical protection without restricting the flexibility or mobility of the bearer. These types of structures are often complex composites and have attracted interest in the field of biomimetics, including the areas of personal armor and protective equipment. Elasmoid fish scales consist of mineral and organic materials, including hydroxyapatite, calcium carbonate and collagen fibers. Scales from pirarucu (*Arapaima gigas*), tarpon (*Megalops atlanticus*), and carp (*Cyprinus carpio*) were fixed, dehydrated, mounted in epoxy and microtomed to expose cross-sections. These sections were analyzed using ESCA and SEM to determine the composite structure and characterize the variations in composition through the scale thickness. ESCA images were obtained for a qualitative evaluation, and spectra from small area analyses provided information for a complementary quantitative analysis. The collagen fibers in the pirarucu were stacked in plys with a rotation angle of 90° between them, while in the tarpon and carp the rotation angle was 75° between successive plys. ESCA images and small area analyses showed the changes in composition between the mineralized limiting layer (LL), the mineral reinforced collagen fibers of the extenal elasmodine (EE) layer, and the collagen fibers of the internal elasmodine (IE) layer.

### AS-ThP4 Ambient Pressure X-ray Photoelectron Spectroscopy of the III-V Semiconductor/Water Interface, ***Pitambar Sapkota***, *S. Ptasinska*, University of Notre Dame

Along with the intense study of semiconductors for promising photovoltaic application, these materials are also used for harvesting solar energy, where energy is stored in the form of chemical fuels. This is through photo-electrochemical (PEC) solar cells, which are being extensively explored recently. Performance and stability of such PEC devices largely depend on the electronic properties and chemistry at the interface of semiconductors and water. Oxidation of the semiconductor surface during operation has been shown to be the major cause of degradation in action and durability of such devices. This research has studied the interactions of water with the III-V semiconductor surface during operando condition using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). The results obtained through this study help to determine the reaction pathway leading to oxidation and its extent on the surface. This knowledge can provide deeper insight into the tuning parameters necessary to obtain better operating and more lasting PEC devices.

### AS-ThP5 Spectroscopic and Structural Studies of Iron Gall Ink, ***Karen Gaskell***, *A.A. Ponce*, University of Maryland, College Park, *L.B. Brostoff*, Library of Congress, *S.K. Gibbons*, *B. Eichhorn*, *P. Zavalij*, University of Maryland, College Park, *C. Viragh*, The Catholic University of America, *S. Alnemrat*, *J. Hooper*, Naval Postgraduate School at Monterey

Iron gall inks were the major writing medium from the middle ages through the 19th Century in the Middle East and Europe, and are present in hundreds of thousands of important cultural heritage objects worldwide, including books, manuscripts and artistic drawings. Iron gall ink depending on its preparation is well known for its potentially corrosive effect on paper or other writing medium, over time, changes in temperature and humidity can accelerate this degradation resulting in the worst case, complete loss of documents. The major ingredients of ion gall ink are iron salts, most often iron sulfate, tannic acids derived from vegetable sources such as gall nuts and gum arabic used as a binder. Despite much research in this area the chemistry of iron gall ink is still poorly understood. Through spectroscopic and structural measurements of synthesized model compounds and authentic documents combined with aging studies, we conclusively show that the main colorant of iron gall ink is an amorphous form of Fe(III) gallate$\cdot x H_2O$ ($x = \sim 1.5$–$3.2$). Comparisons between experimental samples and historical documents by XPS, Raman and IR spectroscopy, XRD, and Mössbauer spectroscopy confirm the relationship between the model and authentic samples.

**AS-ThP7 Multicomponent Patterned Ultrathin Carbon Nanomembranes by Laser Ablation**, ***Daniel Rhinow***, Max Planck Institute of Biophysics, Germany, *N. Frese,* Bielefeld University, Germany, *J. Scherr,* Goethe University Frankfurt, Germany, *A. Beyer,* Bielefeld University, Germany, *A. Terfort,* Goethe University Frankfurt, Germany, *A. Gölzhäuser,* Bielefeld University, Germany, *N. Hampp*, Philipps Universität Marburg, Germany

Carbon nanomembranes (CNMs) are two-dimensional materials obtained by electron beam-induced crosslinking of self-assembled aromatic precursors. Irradiation of aromatic SAMs with low-energy electrons leads to the formation of graphene-like molecular sheets with a thickness of only 1 nm. CNMs made from a single precursor molecule are in principle uniform. We have developed a method for the fabrication of internally patterned CNMs with locally varying chemical and physical properties. Photothermal patterning of SAMs enables the fabrication of arbitrary structured monolayers with lateral dimensions up to centimeters. We have used direct laser patterning to produce patterned aromatic SAMs, which were subsequently converted to CNMs by electron irradiation. Patterned CNMs have been analyzed by helium ion microscopy (HIM), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Our experiments confirm that the structure of patterned CNM is preserved upon electron-induced crosslinking and transfer to different substrates.

**AS-ThP8 Characterization of Laser-Treated Al-Alloy Surfaces**, ***Harry Meyer***, *D. Leonard, A. Sabau*, Oak Ridge National Laboratory

Lightweight materials, such as aluminum alloys, find increasing use in both automotive and aerospace applications. A key requirement for their use is effective surface cleaning and texturing techniques to improve the quality of the structural components. Work at ORNL focuses on the a novel surface treatment method using laser interferometry produced by two beams of a pulsed Nd:YAG laser. Operating at 10Hz of frequency, this technique has been used to clean aluminum surfaces, and at the same time creating periodic and rough surface structures. The influences of beam size, laser fluence, wavelength, and pulse number per spot are currently under investigation. Metallic aluminum is very reactive with atmospheric oxygen and quickly forms a native oxide surface layer. This layer of oxide on the surface can affect further manufacturing processes, such as welding, and must be removed prior to any joining step. Without proper surface preparation, seams and joints are susceptible to increased wear, degradation and, in some cases, catastrophic failure. There are many methods for removing aluminum surface oxides, including mechanical (i.e. abrasive wear) and chemical stripping, generally used for complex part geometries. Despite its effectiveness, chemical stripping also introduces higher costs associated with environmental protection and hazardous-waste management. Aluminum and aluminum alloy surfaces can be cleaned using high-energy laser pulses (nanoseconds to milliseconds range) and is accomplished mainly by surface melting and ablation. This method is a non-contact process without abrasion and chemical impact and the controllability offered by using lasers enables high-precision removal of surface oxides and other contaminants in the range from sub-micrometers to several millimeters. The process being optimized at ORNL is using a 2-beam method that not only cleans the surface for joining but textures the surface in a periodic manner. This poster present preliminary surface characterization results for the cleaning of Al-alloy surfaces. Results from optical and electron microscopies, scanning Auger microanalysis, x-ray photoelectron spectroscopy, and contact angle measurements on as received and laser–treated Al-2024 alloy surfaces will be shown. This abstract has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

**AS-ThP11 Space Weathering Effects on Ceres: Novel Application of Surface Analytical Techniques to Questions in Planetary Science**, ***Gerard Rodriguez Lopez***, *C.A. Dukes, C. Bu*, University of Virginia, *L.A. McFadden*, NASA Goddard, *J-Y. Li*, Planetary Science Institute, *O. Ruesch*, NASA Goddard

**Introduction:** The solar wind plasma continuously streams from the Sun, interacting with the surfaces of airless bodies throughout the solar system. Sulfates, suggested by the thermal emission [1], and carbonates, identified by the 3.4 and 4.0 µm absorption features [2] on the surface of Ceres by NASA's Dawn spacecraft, will be exposed to solar wind $H^+$ and $He^+$ at ~1 keV/amu irradiation. We investigate the stability of these salts under 4 keV $He^+$ irradiation as solar-wind proxy at the low pressure/temperature conditions found in the Main Asteroid Belt.

**Experiment:** Anhydrous $MgSO_4$ and $Na_2CO_3$ powders are pressed into pellets and compositions are confirmed by X-ray diffraction. We measure diffuse optical reflectance prior and subsequent to irradiation through 0.2-2.5 µm (Lambda 1050) and 0.6-16 µm (Thermo Nicolet 670). Pellet samples are then introduced to ultra-high vacuum ($10^{-9}$ Torr) and maintained at 110 K and effects of *in situ* 4 keV $He^+$ irradiation are monitored by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy. Variations in surface composition and chemistry are identified and quantified as a function of fluence.

**Results:** Solar wind type ion irradiation of $MgSO_4$ damages the crystal structure, preferentially removing oxygen along with sulfur. XPS measurements imply the formation of MgO after 5 x$10^{17}$ $He^+$ $cm^{-2}$ (~15,000 years at 2.7 AU); a small shoulder on the sulfur peak suggests the presence of trapped $SO_2$, also confirmed by the IR feature observed at ~7.8 µm with irradiation. McCord et al. (2001) provides a potential decomposition pathway for $MgSO_4$ to $SO_2$ consistent with our observations. We observe secondary ion ejection ($Mg^+$, $MgO^+$, $O^-$, $OH^-$, $H^-$, $S^-$, and $SO^-$ ) from $MgSO_4$ with He-impact, and neutral spectra show loss of $SO_2$. Spectral darkening and reddening in the UV-Vis region is observed by *ex situ* optical spectroscopy after irradiation.

Bright $Na_2CO_3$ deposits darken as a function of solar wind exposure in the visible spectrum on a timescale of 1-10 thousand years. Visible darkening, caused by enhancement in surface Na as C and O are preferentially removed, can be completely reversed by exposure to $H_2O$ vapor. For Ceres' bright regions, this suggests that brightest areas are likely to be the most recent material deposits or the most recently exposed to water.

**Acknowledgements**: We thank the NASA SSW and NSF-Astronomy programs. I thank Dr. Petra Reinke for her support and encouragement.

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3319.

**AS-ThP13 Combustion Soot-derived Carbon Nanostructures: Microscopic and Spectroscopic Investigations**, ***Ich Tran***, *T. Aoki,* University of California, Irvine, *J. Beardslee, C. Moffitt*, Kratos Analytical, Inc.

The formation and fundamental properties of carbon nanostructures from combustion soot are investigated. Chemical and ultrasonic treatments were employed to extract elemental carbon nanostructures from raw soot obtained from combustions of biomass waste materials, as well as from ethylene flames. A combination of transmission electron microscopy and photoelectron spectroscopy/imaging techniques, was used to elucidate the relationships between the formation of combustion soot derived carbon nanostructures and their structural, chemical and electronic properties. These experimental data are correlated to models and mechanisms of soot formation and growth in combustion processes.

**AS-ThP14 Probing the Chemical-State of Zinc centers in unknown Environments: A Comparison of Conventional and Core-core-core Auger Parameter Analyses**, ***William Kaden***, University of Central Florida

Citrus greening is a major problem for the agricultural community in the United States. Afflicted trees typically die within a few years of infection and produce fruit that is green, misshapen, and bitter to the taste. To mitigate the deleterious effects of this epidemic, a Florida-based team of researchers have developed a spray-dispersible bactericide known as Zinkicide$^{TM}$, which consists of zinc-containing nanoparticles capable of entering and freely traversing the phloem-containing vascular system of infected trees to selectively kill bacteria within infected cells. While controlling the size of the particles is of key importance to their membrane transverability, the chemical-state of the zinc centers is believed to be of key importance to controlling the resultant chemical interactions with the bacteria.

Having demonstrated proof-of-concept utility with laboratory-scale quantities of bactericides created from reagent-grade precursors, TradeMark Nitrogen has since begun scale-up efforts using agricultural-grade precursors. Given the importance of chemical-state on the bacteriacidal properties of the nanoparticulates, detailed characterization of the powders is of great importance. Unfortunately, traditional core-level XPS analysis of zinc centers is not sufficient for such characterization due to the relative insensitivity of the most intense transition (Zn 2p), which results in shifts too small to distinguish Zn in chemical compositions as disparate as $Zn^0$ and ZnO for example.

Due to this core-level insensitivity, most reported photoemission analysis of Zn makes use of an associated Auger transition to allow for Wagner plot comparisons to libraries of Zn in known compositions. Such analysis allows for peak assignments through both qualitative and quantitative comparisons with reference data, but is limited in its ability to disambiguate the chemical-states of Zn in environments not perfectly reproducing those of previously measured control samples due to the non-extrapolatable nature of Auger parameter measurements incorporating core-valence-valence transitions. By contrast, appropriately chosen combinations of core-level XPS and core-core-core Auger lines have been shown to provide more reliable estimates of final-state contributions to XPS peak shifts, thereby allowing for direct initial-state interpretation of those shifts (i.e. direct correlation between the extent of the final-state corrected XPS shifts and the degree of oxidation). In this talk, we will present XPS and Auger data sufficient to compare results from both types of analyses on both reference and various Zinkicide$^{TM}$ samples made available for analysis by TradeMark Nitrogen.

## Electronic Materials and Photonics Division
## Room: Central Hall - Session EM-ThP

## Electronic Materials and Photonics Poster Session

**EM-ThP3 Electrolyte-Insulator-Semiconductor (EIS) device with Different Integrated Reference Electrodes for pH Detecting**, ***Rodrigo Reigota***, *J.A. Diniz*, University of Campinas (UNICAMP), Brazil

In this work Electrolyte-Insulator-Semiconductor (EIS) device has been developed for pH measurements. This device operates as a Metal-Oxide-Semiconductor capacitor but instead of having the metal contact electrode, an electrolyte solution and a reference electrode are used to apply voltage. Titanium nitrite (TiN), aluminium (Al) and alumina/aluminium ($Al_2O_3$/Al) were used as reference electrode integrated with EIS device. These materials were deposited by DC sputtering. As dielectric material and sensitive membrane was chosen titanium dioxide ($TiO_2$). This film was obtained by DC sputtering, and was structurally characterized by Atomic Force Microscopy, Raman and Ellipsometry. The structural characterization of $TiO_2$ thin film shows the presence of rutile and anatase crystal structure, physical thickness of 50 nm, refractive index of 2.44 and roughness of 0.4 nm. Was developed MOS capacitors to make the electrical characterization of $TiO_2$ thin films in order to determine the annealing time that leads to the best thin film properties, defined by high dielectric constant value (high-k), lower charge density ($Q_0$/q) and flat-band voltage ($V_{FB}$) around -0.9V. The electrical characterization done by Capacitance x Voltage (CxV) curves revealed that with 15 min annealing the films exhibit the best dielectric constant equals to 133 which is higher than reported in literature. The $V_{FB}$ was -0.6V and $Q_0$/q in the order of $-10^{+12}/cm^2$. The Current x Voltage (IxV) curve shows that the current through the dielectric is approximately $1x10^{-9}$A. With dielectric characterized it was possible to develop the EIS device. From electrical characterization it was possible to test the integrity of the electrodes and determined the sensitivity of the device. For electrical measurement of EIS was used Normalized Capacitance x Voltage curve (CxV curve) using different pH (4, 7 and 10) solutions. From the flat band voltage ($V_{FB}$) of the Normalized CxV curves was possible to determine the sensitivity of the device. The Al and $Al_2O_3$/Al reference electrodes showed a low acid resistance. After measurement with pH 4 the electrodes were corroded. The TiN reference electrode showed to be a very resistant material. This electrode supported the electrical measurements with the three solutions. However, the EIS with the TiN reference electrode showed a low sensitivity of 20mV/pH.

**EM-ThP4 Optical and Magneto-optical Properties of $Zn_{1-x}Co_xO$ / ZnO Hollow Nanospheres**, ***Da-Ren Liu***, *C.J. Weng*, Instrument Technology Research Center, National Applied Research Laboratories

Diluted magnetic semiconductors (DMS) have attracted considerable attention due to their potential applications for spintronic devices, such as spin-valve transistors, nonvolatile memory, and magneto-optical switches. ZnCoO is one of the most promising DMS materials due to its predicted above room temperature ferromagnetism. In this study, ZnO layer was conformally deposited on the surface of polystyrene (PS) nanoshperes with different diameter (100nm~800nm) by atomic layer deposition (ALD). Then the $Zn_{1-x}Co_xO$ ($0.01 < x < 0.1$) coatings were grown on ZnO hollow nanospheres by pulsed laser deposition(PLD). According to the results of high-resolution x-ray diffraction, Co-doping does not change the wurtzite structure of ZnO and the $Zn_{1-x}Co_xO$/ZnO hollow nanospheres are polycrystalline. Photoluminescence spectra and transmittance show an increase of the band gap with increasing Co ion concentration. The temperature-dependent magnetization (M-T) curves of the $Zn_{1-x}Co_xO$/ZnO hollow nanospheres were measured by a superconducting quantum interference device (SQUID) magnetometer and the magneto-optical properties were measured by micro-MOKE spectroscopy. The results show the magneto-optical properties of the $Zn_{1-x}Co_xO$/ZnO hollow nanospheres depend on the Co composition fraction and the size of nanospheres.

**EM-ThP5 Low-k Cryo-etching: Comparison of Four Different High Boiling Point Organic (HBPO)**, ***Romain Chanson***, IMEC, Belgium, *P.L. Lefaucheux, R. Dussart, T. Tillocher*, GREMI, France, *P. Shen, K. Urabe, C. Dussarat*, Air Liquide, Japan, *K. Maekawa*, TEL Technology Center, America, LLC, *K. Yatsuda*, Tokyo Electron Limited, Japan, *S. Tahara*, Tokyo Electron Miyagi Limited, Japan, *J.-F. de Marneffe*, IMEC, Belgium

Low temperature plasma processing is investigated for low damage etching of porous organo-silicate glass ultra-low-k (p-OSG) dielectrics. For additional film protection, in-situ micro capillary condensation is used. This effect allows condensation of a gas precursor into the porous structure. The condensate densifies the porous structure and avoids the plasma by-products to react with the $Si-CH_3$ terminating bonds. In this work, high boiling point organic (HBPO) molecules are studied as reagents for pore filling, enabling for the different gas condensation from -20°C to -50°C. The micro-capillary condensation properties of selected molecules in p-OSG will be compared as well as their desorption kinetic and stability when exposed to a pure $SF_6$ plasma. Using the most promising reagent, patterning tests using a 45nm ½ pitch vehicle and k=2.2 periodic mesoporous oxide low-k dielectric allows to generate vertical trench profiles with good mask selectivity (TiN). A slow kinetic of desorption and a large “Working Window” are critical points for optimal low-k protection.

Acknowledgement: We would like to acknowledge the European commission for its financial support.

**EM-ThP6 Carrier Ion Exchange of $Na_2O-Fe_2O_3-P_2O_5-SiO_2$ Glass-Ceramics**, ***Yoshikazu Kaji***, *N. Yoshida, T. Okura*, Kogakuin University, Japan

Our group has developed $Na^+$-superionic conductive Narpsio (typically represented as a general formula of $Na_3RP_ySi_{3-y}O_9$, R=rare earth) glass-ceramics, as analogues of $Na_5RSi_4O_{12}$ (N5)-type $Na^+$-superionic conductors, and it was revealed that these showed excellent ionic conductivity up to $\sim 10^{-1}$ S/cm, which is comparable to those of the conventional ceramic $Na^+$-conductor such as b- and $b^2$-aluminas and NASICONs. Recently we achieved two important replacements, that is, R with Fe, and carrier $Na^+$ with $H^+$. The replacement of R with cheap and rich Fe is important in terms of cost and amounts of resources. The carrier ion exchange of $Na^+$ with $H^+$ will spread its applications, such as a fuel cell.

In this study, $Na_{4.9}FeP_{0.1}Si_{3.9}O_{12}$ glass-ceramics of N5 phase was prepared at first, and then, exchange of carrier $Na^+$ ion with $H^+$ was tried in several conditions.

$Na_{4.9}FeP_{0.1}Si_{3.9}O_{12}$ glass-ceramics of N5 phase was prepared by melt-quenching and glass-crystallization method. Ion exchange experiment was carried out as follows; while monitoring with pH meter, prepared glass-ceramics was immersed into HCl aq. with/without NaCl at room temperature.The obtained samples were characterized by X-ray diffraction analyses (XRD), thermogravimetry-differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC).

XRD measurement indicated that glass-ceramic $Na_{4.9}FeP_{0.1}Si_{3.9}O_{12}$ of N5 phase was successfully prepared. After ion exchange without addition of NaCl, unknown phase was appeared in XRD pattern, and this change could not be suppressed by changing concentration of HCl aq. A possible explanation against this change is due to dissolution of bonding $Na^+$ in addition to carrier $Na^+$. After ion exchange with addition of NaCl, unknown phase was disappeared, although slight decrease in crystallinity was observed.

Glass-ceramic $Na_{4.9}FeP_{0.1}Si_{3.9}O_{12}$ of N5 phase was successfully prepared and replaced carrier $Na^+$ ion with $H^+$ without significant changes in crystallinity under the conditions of ion exchange with addition of NaCl. Detail of experiments and thermodynamic data will be discussed in the presentation.

**EM-ThP7 Defect Doping ZnO Thin-Films with $\gamma$ - Radiation**, ***Seth King***, *K.C. Slezak*, University of Wisconsin - La Crosse, *S.E. Chamberlin*, Lawrence University, *S.M. Lantvit*, University of Wisconsin - La Crosse

Sputter deposited ZnO thin films have been exposed to prolonged high energy gamma radiation in a 400 Ci $^{137}Cs$ irradiator to examine the impact of such exposure on the optical, structural, and electronic properties of this technologically important wide-bandgap semiconductor . While many studies have shown that ZnO is radiation hard to proton and electron damage [1,2], only one has investigated the effects of exposure to high-energy photons, and not in an iterative manner [3].

UV-Vis spectrometry and spectroscopic ellipsometry show little variation in the over-all transmittance, optical constants, or optical bandgap of the irradiated films. Continued exposure shows a decrease in the films’ resistivity, which, along with supporting x-ray photoelectron spectroscopy data, suggests that induced O-vacancies are acting as donors to dope the irradiated films.

References:

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**EM-ThP8 Design and Synthesis of Precursors for Photoassisted Chemical Vapor Deposition**, ***Christopher Brewer***, *O. Hawkins,* University of Florida, *B. Salazar, A.V. Walker,* University of Texas at Dallas, *L. McElwee-White*, University of Florida

Chemical vapor deposition (CVD) is a potentially attractive technique for the metallization of organic thin films. However, thermal CVD processes often require high temperatures which are incompatible with organic substrates. Photochemistry provides an alternative means of initiating precursor decomposition without heating the substrate. Readily available Ru precursors, including ($\eta^3$-allyl)Ru$(CO)_3$X and CpRu$(CO)_2$X (X = Cl, Br, I), have been used to deposit Ru on functionalized self-assembled monolayers (SAMs) by means of photochemical CVD as a model system for deposition of metal on a thermally sensitive substrate. Carboxylic acid-, hydroxyl- and methyl-terminated SAMs were used to explore the effects of surface functionality on deposition and the presence of Ru on the SAMs was confirmed by HR TOF SIMS. Preliminary experiments have shown that an attractive precursor for photoassisted CVD will be volatile, have an acid sensitive functionality and have a reasonable quantum yield for ligand loss. Synthesis of the precursors, determination of the quantum yields and deposition of Ru onto the functionalized SAMs will be discussed.

**EM-ThP9 Electrical and Mechanical Improvements with a Non-Thermal Curing Process for Porous SiCOH using Combined Ultraviolet and Vacuum-Ultraviolet Radiation**, ***Sang-heum Kim***, *J. Blatz, W. Li, H. Zhang, D. Pei, T. Guo, X. Zhou,* University of Wisconsin-Madison, *Y. Lin, H. Fung, C. Chen,* National Synchrotron Radiation Research Center, Taiwan, Republic of China, *S.W. King,* Intel Corporation, *Y. Nishi,* Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Porous SiCOH films are rapidly emerging as preferred interplay dielectric materials in semiconductor fabrication because of their ultra-low dielectric-constant properties. Ultraviolet (UV) light on organosilicate thin films in post-deposition treatments initiates to photo-chemical process by nano pores generators (porogens) and form a network to improve mechanical properties of the dielectrics. A simple and cost-saving method of improving not only the mechanical property but also electrical property was found by combined with two different UV exposure energies called UV/Vacuum Ultraviolet (VUV) photons curing without the need for heating the dielectric [1] The goal of this work is to choose the best combined UV/VUV photon energies and to investigate beneficial effects that lower the dielectric constant, minimize damage, and increase the elastic modulus of low-k dielectrics as a function of the fluence of the UV/VUV curing photons. The following measurements were made. (1) We exposed SiCOH films samples with UV/VUV photon energies ranging from 4.5 to 8.9 eV from a beamline at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. (2) Using both nanoindentation and Time-Dependent Dielectric Breakdown (TDDB) measurement, we found the most beneficial energies (usually 2) for improving both electrical and mechanical properties could be found from VUV spectroscopic measurements. (3) We exposed the same SiCOH films at the same beamline using two combined photon energies with four different fluences from 5 x 10^14 photons/cm2 and 10^16 photons/cm2. (4) We measured TDDB and the nanoindentation after exposure. We show that this method can be applied to different porous SiCOH films, so that we can overcome drawbacks of UV curing and improve the properties of these dielectrics at room temperature.

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**EM-ThP10 The Effects of Cesium Ion Implantation on the Mechanical and Electrical Properties of Porous SiCOH Low-k Dielectrics**, ***Weiyi Li***, *D.I. Benjamin, J. Chang,* University of Wisconsin - Madison, *Q. Lin,* IBM Research Division, T.J. Watson Research Center, *S.W. King,* Intel Corporation, *J.L. Shohet*, University of Wisconsin - Madison

In this work, we investigate the effects of cesium (Cs) ion implantation on both porogen-embedded and UV-cured (porous) SiCOH films. It has been shown in past work that Cs doping has benefits for either spin-on low-*k* dielectrics[1] or PECVD deposited non-porous SiCOH low-*k* dielectrics.[2] For porogen-embedded SiCOH, it was found that Cs ion implantation can greatly improve the elastic modulus up to twice its original value . It can also increase the time-zero dielectric breakdown (TZDB) strength. It also leads to an increase in the k-value for medium and high Cs doses, but for low Cs doses the k-value decreases compared with its pristine counterpart. These effects can be understood by examining the changes in Si-$CH_3$ bonds and Si-O bonds . For UV-cured SiCOH, it was found that Cs ion implantation does not modify the elastic modulus. This also leads to lower TZDB field strength and much higher k-values than its pristine counterpart. This treatment is shown to have a potential to help solve the problem between the demand for lower k-values and the concomitant weak mechanical strength of SiCOH.

This work was supported by the Semiconductor Research Corporation under contract 2012-KJ-2359.

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**EM-ThP11 The Effect of Proton Radiation on ALD $HfO_2$ Films and $HfO_2$ base RRAM**, ***Panpan Xue***, University of Wisconsin-Madison, *Z. Wang,* Stanford University, *T. Chang,* University of Wisconsin-Madison, *Y. Nishi,* Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Hafnium oxide($HfO_2$) is one of the most popular dielectric materials for RRAM. Changes of the defect concentrations of $HfO_2$ may affect the resistive-switching mechanism of RRAM. In this work, in order to investigate the effects of proton radiation, (1) atomic-layer-deposited (ALD) $HfO_2$ blanket films deposited on a Si substrate and (2) $HfO_2$ base RRAM were exposed to proton. After exposure, electron spin resonance and FTIR measurements were made on the $HfO_2$ blanket film, forming voltage and I-V characteristics were measured on the RRAM cell. The samples were exposed to proton radiation with a range of energies from 10 to 300keV. H ion implantation was used as the proton source. ESR measurements showed that after 300keV proton exposure, the defect concentration of Si dangling bond increased. Besides, all of the fresh pristine RRAM cells need to be formed, the forming voltage is approximately 3.4 ~ 3.65V. However, a number of the low-energy proton-exposed samples are set after exposure: about 50% of the 10keV proton exposed RRAM samples are set to the “on” state after irradiation. The 300keV proton-exposed RRAM samples were not formed or set after proton exposure, but the needed forming voltage decreased and breakdown occurred at a lower voltage. This is consistent to a TRIM simulation result, after low energy exposure, some of the H ions are seen to stay in the $HfO_2$ films and generate conductive filaments that set the dielectric film to the low resistance state. However, 300keV protons have just enough energy to pass through the dielectric film. In addition, the high-resistance state (HRS) current of just-formed 300keV exposed RRAM is about 100 times higher than that for pristine RRAM. We conclude low-energy protons have a significant effect on the forming process of RRAM. However, higher-energy protons change the resistance of the HRS instead.

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**EM-ThP12 Measurement of the Depth of Plasma Damage caused by VUV Photons and Oxygen Radicals using X-ray Reflectivity**, ***Ha Nguyen***, *F.A. Choudhury,* University of Wisconsin-Madison, *C. Lee,* National Tsing Hua University, Taiwan, Republic of China, *Y. Lin, H. Fung, C. Chen,* National Synchrotron Radiation Research Center, Taiwan, Republic of China, *J. Blatz, D.I. Benjamin, W. Li, J.L. Shohet*, University of Wisconsin-Madison

During plasma processing, dielectric films used in the semiconductor technology are often exposed to large doses of vacuum ultraviolet (VUV) radiation and free radicals that can damage the dielectric material. In this work, we utilize specular x-ray reflectivity to measure the depth of damage of dielectric films as a function of energy of VUV photons and various doses of oxygen radicals. First, we examine the VUV-absorption spectrum of low-k organosilicate glass (OSG) using specular X-ray reflectivity (XRR). Low-k SiCOH films were exposed to synchrotron VUV radiation with energies ranging from 7 to 25 eV and the density depth profile of the VUV-irradiated films were extracted from the fitting of the XRR experimental data. The results show that the depth of the VUV-induced damage layer is a function of photon energy. Between 7 and 11 eV, the depth of the damaged layer decreases sharply from 110 nm to 60 nm and then gradually increases to 85 nm at 21 eV. The maximum VUV absorption in the OSG films occurs between 11 and 15 eV. Next, $SiO_2$ dielectric films were exposed to oxygen plasma in an electron cyclotron resonance plasma reactor and XRR measurements were made in order to determine the depth of damage as a function of oxygen-radical dose. It was found that the depth of damage increases as a function of plasma exposure time and eventually saturates to ~ 66 nm after about 30 minutes of oxygen-plasma exposure. This work shows that XRR damage depth profiling can be a very effective, non-destructive tool to determine the penetration depth of VUV photons and other plasma reactive species in dielectric films [1].

This work was supported by the Semiconductor Research Corporation under contract 2012-KJ-2359.

[1] Faraz A. Choudhury *et al*. "Oxygen radical transmission through and damage to freestanding single and multilayer dielectric films" AVS 64th International Symposium & Exhibition, Tampa, Florida (2017).

### EM-ThP13 Oxygen Radical Transmission through and Damage to Freestanding Single and Multilayer Dielectric Films

***Faraz Choudhury***, *G. Sabat, M.R. Sussman,* University of Wisconsin-Madison, *Y. Nishi*, Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

During plasma processing, dielectric films are exposed to a high concentration of free radicals that can affect the processing conditions and the properties of materials exposed to the plasma. Measuring the absorption lengths and penetration depths of free radicals is critical in order to determine their effects on the dielectric materials. Using radical-sensitive fluorescent dyes and free-standing films, the transmission of oxygen radicals through silicon nitride and silicon dioxide dielectric films is measured. The absorption length of the oxygen radicals is determined by measuring the number of transmitted radicals as a function of the thickness of the freestanding films. For silicon nitride films, the absorption length was found to be 33 nm for 15-minute oxygen plasma exposure. The absorption lengths increased to 37 and 40 nm for 30 minute and 45-minute plasma exposures, respectively. FTIR measurements showed a decrease in Si-N bond concentration after plasma exposure and a subsequent appearance of Si-O-Si bonds. In addition, the density vs. depth profiles of the pristine and plasma exposed films were obtained from specular x-ray reflectivity (XRR) measurements which showed that the plasma exposure forms a silicon oxynitride-like layer on the surface of the film which has a lower density than silicon nitride. The increase in absorption length with plasma-exposure time is attributed to the formation of the surface layer. In silicon dioxide films, the absorption length of oxygen radicals was found to be ~70 nm after 20 minutes of plasma exposure. After 30 minutes of plasma exposure under the same conditions, the absorption length was reduced to ~66 nm. XRR and FTIR measurements both reveal that the oxygen plasma exposure leads to further oxidation of the silicon dioxide film and the formation of a denser surface layer which restricts the transmission of the radicals through the film.

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### EM-ThP15 Effect of Proton Irradiation on Device Characteristics of Bottom Gate ZnO Thin Film Transistors with Sol-Gel Derived Channel Layers

***Kosala Yapabandara***, *V. Mirkhani, S. Wang, M.P. Khanal, S. Uprety,* Auburn University, *M.H. Sk,* Qatar University, Qatar, *A. Ahyi, T. Isaacs-Smith, M.C. Hamilton, M. Park,* Auburn University

ZnO has been widely studied due to its promising material properties as a wide energy bandgap semiconductor, optical transparency, and high carrier mobility for thin film transistor (TFT) technology. Solution-based ZnO can easily be deposited on large areas of substrates at low temperatures, which makes this material a good candidate for commercial device manufacturing. Moreover, ZnO exhibits a higher radiation hardness compared to semiconductors such as Si, GaAs, and GaN. However, it is not entirely understood why ZnO shows superior radiation hardness over GaN.

In this work, we report the device performance analysis of solution derived ZnO TFTs upon irradiation of 100 keV proton with $10^{14}$ cm$^{-2}$ fluence. A comprehensive analysis of unirradiated and irradiated samples was performed to elucidate the proton irradiation effect on ZnO TFTs. The room temperature photoluminescence analysis showed a slight reduction in intensities of near-band-edge UV peak and visible luminescence band while the peak positions and the full-width half maximum (FWHM) are unchanged upon irradiation. This implies that negligible damage has occurred in the ZnO channel layer due to the proton irradiation. From transfer characteristics analysis, it was observed that the reduction in the drain current ($I_D$ ) at high drain-source voltages ($V_{GS}$) regime is less than an order of magnitude, which also suggests minimal irradiation damage to the ZnO lattice. However, the shift in $V_{ON}$ and an enhancement in subthreshold swing (SS) after the proton irradiation were observed, which is believed to be produced by radiation-induced electron-hole pair production in the $SiO_2$ layer. Multiple peaks in incremental mobility ($\mu_{inc}$) variation with $V_{GS}$ and a plateau in low-frequency C-V curve were observed in unirradiated samples. A model was proposed to explain these abnormalities. It is reasonable to think that a significant number of defects is introduced into sol-gel derived ZnO channel during the deposition process. Since our deposition process requires more that one spin coating run, ZnO-ZnO interlayer interfaces will be formed. It was hypothesized that the depletion regions are created by oxygen-related trap centers at the ZnO-ZnO interlayer interfaces. It was conjectured that the disappearance of multiple peaks in $\mu_{inc}$ and the plateau in low-frequency C-V curve upon proton irradiation might be the result of the reduction of the depletion layer in the proximity of ZnO-ZnO interlayer interface.

### EM-ThP16 Characterization of the Buried MgO/Al Interfaces in Multilayer Heterostructures used as Photocathodes with Hard X-ray Photoelectron Spectroscopy

***Jeff Terry***, Illinois Institute of Technology

Early research and development of photocathode material was based on characterizing compounds with low work function and high quantum efficiency. Recent theoretical and experimental work has shown that the metal-insulator junctions can give rise to changes in the band structure at the interface, which in turn leads to a change in work function and quantum efficiency.

In addition to concerns about work function and quantum efficiency, many modern photoinjector designs also require low beam emittance. Beam emittance is an intrinsic property of the photocathode, therefore it is important to be able control the growth and quantify the factors that lead to such growth. Nemeth [Phys. Rev. Lett. 104, 046801 (2010)] used DFT to model metal- insulator multilayer junction. The model indicate that it is possible to reduce the emittance of the photoemitted beam. Velazquez et al [Appl. Surf. Sci. 360, 762 (2016)] has demonstrated that the work function of lab grown thin film multilayers had trends that match the theory. However the model predicted an exponential decrease of work function, but data suggests a linear decrease.

It has been suggested that the surface roughness of the lab grown thin film multilayers might be the main cause of the deviation from the theory. Thin films are synthesized with a custom build dual laser PLD system, and the surface roughness is systematically altered by growing at different substrate temperature. We utilized a Hard X-ray Photoelectron Spectroscopy (HAXPES) system on the MRCAT undulator beamline at the Advanced Photon Source to characterize the MgO/Ag multilayers to better understand the chemistry at the interface. Understanding the reactivity, can help us better understand how the growth transitions from uniform to rough with increasing layer number.

### EM-ThP17 Gamma-Ray Irradiation Effects on HfO2 RRAM Studied via EDMR

***Duane McCrory****, P.M. Lenahan,* Penn State University, *D. Nminibapiel, D. Veksler, J.T. Ryan, J.P. Campbell*, National Institute of Standards and Technology

Resistive Random Access Memory (RRAM) is a leading candidate for future non-volatile memory applications. These devices may be extremely useful for space applications. However, at the present time there is virtually no direct experimental evidence identifying the atomic scale defects involved in RRAM radiation damage or the underlying atomic scale conduction mechanisms. One of the most promising systems for RRAM is $HfO_2$ metal-insulator-metal based devices. In these devices, it is believed that the switching mechanism is derived from filamentary conduction paths within the oxide. One widely accepted mechanism involves the migration of oxygen vacancies within the transition-metal-oxide insulator, forming the conducting filament [1]. However, to the best of our knowledge, no direct experimental evidence establishes this transport mechanism.

By far the most powerful analytical tool available for identifying atomic scale defects is electron paramagnetic resonance (EPR). Using conventional EPR, Ryan et. al. have identified two atomic scale defects directly involved in gamma-irradiation damage; an $O^{2-}$ coupled to a hafnium ion, and an oxygen vacancy center [2]. However, conventional EPR is not sensitive enough to observe defects within the RRAM. We must look elsewhere to identify the defects and transport mechanisms. The most sensitive technique for identifying these defects is electrically detected magnetic resonance (EDMR) [3].

In this study we have subjected the TiN/Ti/$HfO_2$/TiN RRAM devices to 1 MRAD of $^{60}$Co gamma irradiation. These 100x100 nm devices are cross-point type RRAM with 5nm thick $HfO_2$. We have made EDMR measurements before and after gamma irradiation. We observe the radiation induced generation of two strong spectra that appear in both the in-phase and quadrature. We believe that this response is due to two different trap assisted tunneling mechanisms within the oxide. Both spectra appear to be reasonably consistent with the earlier observations of Ryan et. al [2]. A DFT study by Muñez et. al. linked this defect earlier observed for the Ryan et. al. as an oxygen vacancy [4]. DFT calculations by Bradley et. al. have linked two di-vacancy sites near the middle of the $HfO_2$ bandgap that may contribute to transport in $HfO_2$ [5]. Our results provide strong evidence linking electronic transport and radiation damage mechanisms to transport through oxygen vacancy related centers.

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**EM-ThP19 Defect Dependent Luminescence Dead Layers in CdS and CdSe**, ***Richard Rosenberg***, Argonne National Laboratory

CdS and CdSe are often used in optoelectronic devices whose effectiveness may be dictated by defects in the near surface region. Luminescence is one of the main tools for studying such defects. The energy dependence of the X-ray excited optical luminescence (XEOL) spectra of these materials enables the extraction of the depth-dependence of the defect distribution.[1] Normal and time-gated XEOL spectra were obtained from these materials in the X-ray energy range 600 to 1500 eV. The individual components of each spectrum were extracted using curve fitting techniques. Each component's energy-dependent intensity was fit to a "dead layer" model.[2] We find that the results can best be understood in terms of a luminescence dead layer whose width depends on the position of the defect level in the band gap.

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**EM-ThP20 High Breakdown Voltage (-201) β-$Ga_2O_3$ Schottky Rectifiers**, ***Jiancheng Yang***, *S.H. Ahn, F. Ren, S.J. Pearton*, University of Florida

A reverse breakdown voltage of 1600 V was demonstrated for Schottky diodes without edge termination fabricated on 10 µm epitaxial β-$Ga_2O_3$ grown bulk conductive substrate. $Ga_2O_3$ has a theoretical Baliga figure of merit (defined as $V_B^2/R_{ON}$, where $V_B$ is the reverse breakdown voltage and $R_{ON}$ is the on-state resistance) significantly higher than more familiar wide bandgap semiconductors, due mainly to its larger bandgap (~4.5-4.8 eV) compared to that of 4H or 6H-SiC and GaN (~3.0-3.4 eV). The theoretical breakdown electric field is ∼8 MV/cm, with experimental demonstrations as high as 3.8 MV/cm and this is already higher than the bulk critical field strengths of both GaN and SiC. In this work, the β-$Ga_2O_3$ Schottky barrier diodes were fabricated in a vertical geometry structure consisting of Ni/Au rectifying contacts without edge termination on Si-doped epitaxial layers (10 µm, n~ $4\times10^{15}$ $cm^{-3}$) grown on Sn-doped bulk $Ga_2O_3$ substrates with full area Ti/Au back Ohmic contacts. The reverse breakdown voltage, $V_{BR}$, was a function of rectifying contact area, ranging from 1600V at $3.1\times10^{-6}$ $cm^2$ (20µm diameter) to ~250V at $2.2\times10^{-3}$ $cm^{-2}$ (0.53 mm diameter). The current density near breakdown was not strongly dependent on contact circumference but did scale with contact area, indicating the bulk current contribution was dominant. The lowest on-state resistance, $R_{on}$, was 1.6 mΩ-$cm^2$ for the largest diode and 25 mΩ.$cm^2$ for the 1600V rectifier, leading to a Baliga figure-of-merit ($V_{BR}^2/R_{on}$) for the latter of approximately 102.4 MW·$cm^{-2}$. The on-off ratio was measured at a forward voltage of 1.3V and ranged from $3x10^7$ to $2.5x10^6$ for reverse biases from – 5 to -40 V and showed only a small dependence on temperature in the range 25-100°C. The Schottky barrier height decreased from 1.1 at 25°C to 0.94 eV at 100°C, while the ideality factor increased from 1.08 to 1.28 over the same range. The reverse recovery time was 26 ns for switching from +5V to -5V. These results represent another impressive advance in the quality of bulk and epitaxial β-$Ga_2O_3$.

**EM-ThP21 Inelastic Electron Tunneling Spectroscopy and Electron Conduction Mechanisms of Porphyrin Molecular Junctions**, ***Teresa Esposito***, *P.H. Dinolfo, V. Meunier, K.M. Lewis*, Rensselaer Polytechnic Institute

In order to achieve nanoscale electronic devices beyond the 10 nm limit predicted by Moore's Law, molecular electronic devices are being studied as alternatives to circuit elements such as diodes, switches, and transistors. Porphyrin molecules are of interest because they have been shown to exhibit switching and diode behavior. In addition, shorter porphyrins (2-3 nm) can be used as interconnects because their low attenuation factors ($\beta<0.01$ $nm^{-1}$) allow for long range electron conduction. Our work investigates three types of short porphyrins: a free base porphyrin, and porphyrins with either a zinc or an iron atom ligated to the porphyrin ring. Nanostructures are formed by depositing porphyrins into a 3-5 nm gap created by electromigration of a 30x50 nm gold nanowire to create a molecular junction (MJ). In order to determine the mechanism for electron conduction through these porphyrin MJs, temperature dependent current-voltage (I/V) studies have been performed and compared to existing models of electron transport, and are shown to be direct tunneling. Inelastic electron tunneling spectroscopy (IETS), which is the second derivative of I/V, is measured simultaneously at temperatures from 4.2 to 300 K. IETS is used to verify the presence of a molecule in the gap. Peaks in the spectra indicate the excitation of a vibrational mode, which are compared to Fourier transform infrared spectroscopy, surface enhanced Raman spectroscopy, and theoretical density functional theory calculations.

**EM-ThP22 Welding of Metal Nanowire Networks Using Eddy Current Method**, ***JiSoo Oh***, *D.I. Sung, D.S. Kim, K.H. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Silver nanowire (AgNW) network is one of the most promising candidates to replace indium tin oxide (ITO) as transparent conductors among several candidates such as carbon nanotubes, graphene, metal grid, conducting polymer, etc. AgNW has lots of advantages, for example, AgNW not only has inherent high electrical conductivity and high transparency but also can be easily fabricated by using various methods on the flexible substrates. Despite these advantages, AgNW has its limitations due to high surface roughness and low adhesion problem. Especially, a high contact resistance between AgNW from the coating of polyvinylpyrrolidone (PVP) due to the loose contact between individual AgNWs is a critical issue to be resolved.

In order to overcome these problems, we constructed an inductive coil system that generates eddy current and welded nanowires with different operating frequencies. This method welds only the junction between the nanowires without heating the substrate due to higher resistance at the junction. Using this method, the various metal nanowires such as Ag and Cu nanowires were successfully welded by reducing the sheet resistance about 67% without changing the optical transmittance, and it was confirmed that it can be applicable to various flexible dielectric substrates such PET substrates. Due to the local melting at the junction, the decrease of surface roughness could be also confirmed by surface image measurement. In addition, no significant change in resistance by bending test and adhesive test was observed due to the successful welding of the junction part of the nanowire, thereby improving the properties of the nanowire networks. This welding method is believed to be applicable to all kinds of metal nanowires without heating or touching of the substrate and on a large area at short process time and at low-cost.

**EM-ThP23 Deep Ultraviolet Light Source with Carbon Nanotube based Electron Beam Pumping**, ***KyuChang Park***, *S.T. Yoo*, Kyung Hee University, Republic of Korea

Deep ultaviolet (UVC) light sources were fabricated with carbon nanotube based electron beam pumping technique. Anode materials for UVC generation made by home-made fabrication process with Zn & Si mixture and irradiated with the carbon nanotube based cold cathode electron beam (C-beam). The C-beam fabricated with triode structure with metal mesh gate electrode and CNT cold cathode. The C-beam shows more than 90% electron transmittance through gate electrode and more than 10 mA anode current in DC operation.

For UVC light generation, anode semiconducting layer formation process is very important and should be optimized with electron beam irradiation current density. The UVC light intensity strongly related on the annealing conditions of anode layer and optimized to 1,000 degree celcius and nitrogen ambient. To reduce the power consumption, C-beam irradiated with DC pulse driving.

UVC light source with novel anode and C-beam irradiation technique shows emission peak at 208 nm, 226 nm, and 245 nm. The emission peak depend on the anode fabrication process and C-beam irradiation coditions. More detail on the UVC light fabrication with C-beam irradiation will be presented

**EM-ThP24 An Unexpected Trend between Metal Work Function and Contact Resistance to Germanium Telluride**, ***Kayla Cooley***, *H. Simchi, H. Aldosari, J. O'Neil, S-Y. Yu, A. Molina, S.E. Mohney*, The Pennsylvania State University

Germanium telluride is an emerging phase change material (PCM) that has shown exceptional promise for radio frequency (RF) switch technology. When an appropriate heating schedule is applied, this material quickly transitions between crystalline (conductive ON state) and amorphous (highly resistive OFF state). Currently, the contact resistance ($R_c$) contributes 20-50% of the ON-state resistance of the switch and significantly degrades RF circuit performance. Low-resistance Ohmic contacts that are able to withstand the thermal cycling necessary for changing the phase of GeTe are therefore necessary for successful implementation of GeTe-based RF switches .

We investigated selected contact metals (Ti, Sn, Cr, Mo, Ni, Au, and Pt), resulting in $R_c$ from 0.004 to 0.036 Ω-mm (specific contact resistances of 5 x $10^{-9}$ to 4 x $10^{-7}$ Ω-$cm^2$) . We also characterized surfaces and interfaces using X-ray photoelectron spectroscopy and transmission electron microscopy with energy dispersive spectroscopy. The lowest $R_c$ values (0.004 ± 0.001 Ω-mm) were achieved using Sn and Mo-based contacts, with $R_c$ ranked according to the first metal deposited as follows: Mo or Sn < Cr < Ti < Au < Ni < Pt. This trend is surprising, as high work function metals, like Au and Pt, would be expected to provide lower $R_c$ values to *p*+ GeTe.

In the case of Sn-based contacts, low $R_c$ can be attributed to a beneficial interfacial reaction that formed SnTe upon deposition at the contact interface; however, for Mo-based contacts, no such interfacial reaction was observed.

Chemical reactions at the interface were not always favorable. In the case of Pt and Ni, the formation of metal tellurides resulted in very high $R_c$. Thermal stability of all contact metals was also investigated up to 200 ºC for 30 min. While Sn and Mo-based contacts performed just as well after annealing, $R_c$ of most other contacts increased. Te sublimation was a common source of thermal instability, with Te crystallites forming on the sides of contacts and within the gap.

**EM-ThP25 RF Loss Improvement of GaN-HEMTs Grown on Silicon by Reduction of The Inversion Channel at Si Interface**, ***TienTung Luong***, *Y.H. Chen, J.Y. You, S. Chang, Y.T. Ho, Y.C. Lin,* National Chiao Tung University, Taiwan, Taiwan, Republic of China, *J.C.S. Woo,* University of California, Los Angeles, *E.Y. Chang,* National Chiao Tung University, Taiwan, Taiwan, Republic of China

Regarding the unique characteristics (high breakdown field, high power density, high efficiency, and broadband) GaN are now broadly recognized as a key technology for many applications. In particular, GaN-based HEMTs are able to operate at high power, high frequencies, and high temperatures, exhibiting various excellent characteristics superior to those of conventional Si-based semiconductors. GaN-HEMTs on Si technology is expected to drastically reduce the fabrication cost. However, one of the main issues is the parasitic loss that can adversely impact the RF device performances. A free-electron inversion channel, which is caused by the positive piezoelectric charge at the AlN/Si interface induced by the piezoelectric field in the tensile AlN grown on Si, plays a critical role in the RF losses. An adoption of a low-temperature AlN near Si interface induces an unintentionally carbon-doped layer acting as a negatively fixed charge layer that is able to compensate for positive piezoelectric charge resulting in the improvements of both the RF losses and the leakage.

**EM-ThP26 The Photoelastic Coefficient $P_{12}$ of $H^+$ Implanted GaAs as a Function of Defect Density**, ***Andrey Baydin***, *H.T. Krzyzanowska, R. Gatamov, N.H. Tolk,* Vanderbilt University

The photoelastic phenomenon has been widely investigated as a fundamental elastooptical property of solids. This effect has been applied extensively to study stress distribution in lattice-mismatched semiconductor heterostructures. GaAs based optoelectronic devices (e.g. solar cells, modulators, detectors, and diodes) widely used in space probes are subject to damage arising from energetic proton $H^+$ irradiation. For that reason, the effect of proton irradiation on photoelastic coefficients of GaAs is of primary importance to space applied optoelectronics. However, there yet remains a lack of systematic studies of energetic proton induced changes in the photoelastic properties of bulk GaAs. In this work, the $H^+$ energy and fluence chosen for GaAs implantation are similar to that of protons originating from the radiation belts and solar flares. We present the depth-dependent photoelastic coefficient $P_{12}$ profile in non-annealed $H^+$ implanted GaAs obtained from the analysis of the time-domain Brillouin scattering spectra. The depth-dependent profiles are found to be broader than the defect distribution profiles predicted by Monte Carlo simulations. This fact indicates that the changes in photoelastic coefficient $P_{12}$ depend nonlinearly on the defect concentrations created by the hydrogen implantation. These studies provide insight into the spatial extent to which defects influence photoelastic properties of GaAs.

**EM-ThP27 Manipulation of Elliptical Polarization and Modulation of Optical Activity using Terahertz Stereo-metamaterial Reflectors**, ***Elizabeth Philip***, *S. Pal, S.E. Stephens, P. Kung, S.M. Kim,* The University of Alabama

Metamaterials (MMs) are playing a vital role in the development of the field of photonics. These are artificial materials made by repeated arrays of meta-atoms of subwavelength size, and can be controlled to manipulate the electromagnetic (EM) waves interacting with them. With appropriate designing of these meta-atoms, it is possible to achieve unique EM properties such as perfect absorption, negative permittivity, negative permeability, electromechanically induced transparency, etc. Recently, in terahertz (THz) frequency regime, MMs are being employed to replace conventional polarization converters. Conventional polarizers, retarders, rotators, etc. are usually made using dichroic crystals and optical gratings that are bulky, less efficient and operate in narrow bandwidths. Whereas with MMs they can be made thin, compact, easily combinable and even flexible. Much of the current THz polarization converters made of MMs function only in the transmission mode [1]. Though there are a few that function in the reflection mode, these are mostly linear polarization converters [2]. Evidently, there is a lack of linear to elliptical or circular reflective polarizers in the THz regime. In this work, we take advantage of an interesting category of MMs called stereo-metamaterials (SMMs) to develop a linear to elliptical polarization converter. SMMs utilize the same meta-atom, but are arranged at different spatial positions. They are analogous to stereo-isomers, which are molecules constituting of the same atoms but have different spatial arrangements. Six separate devices with varying spatial arrangements are first optimized through simulations with finite element method using Comsol. By tailoring the spatial arrangement of the meta-atom, we manipulate the polarization of the reflected light to become elliptically polarized, achieving a maximum ellipticity angle of 20.5° at 0.240 THz. Furthermore, we modulate the optical activity of the device, and a pure optical rotation of 37.0° at 0.246 THz is attained from the simulation results. The devices are fabricated using standard photolithography techniques and their linear to elliptical polarization conversion and optical activity is successfully verified through THz ellipsometry measurements. The device sensitivity to incident polarization modulation and its corresponding reflective phase retardation response is also analyzed. Lastly, the influence of the dipole coupling and current distribution is studied in order to explain the microscopic origin for the manipulation of the reflected light. Such SMM with linear to elliptical polarization conversion and optical activity modulation properties in the reflection mode has promising applications in THz sensing and communication devices. [1] J.W. He, Z.W. Xie, S. Wang, X.K. Wang, Q. Kan, Y. Zhang, Journal of Optics. 2015;17(10):8. [2] N.K. Grady, J.E. Heyes, D.R. Chowdhury, Y. Zeng, M.T. Reiten, A.K. Azad, et al. Science. 2013;340(6138):1304-7.

## Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
## Room: Central Hall - Session HC-ThP

## Fundamental Discoveries in Heterogeneous Catalysis Poster Session

**HC-ThP2 Auger Electron Spectroscopy Analysis of Fresh and Aged Alumina Supported Ag Catalysts**, ***Dennis Paul***, *J. Newman,* Physical Electronics, *W. Suchanek,* Scientific Design Company, Inc.

Auger Electron Spectroscopy is a well known surface analysis method optimized for characterization of very small features. The technique has an inherent depth of analysis of ~5 nm and can provide analysis of features as small as ~20 nm. While Auger works well on conducting and semiconducting materials, it is much more challenging to analyze insulating samples due to uncompensated charge buildup that occurs during electron bombardment. Thus, for catalyst analysis on insulating supports (typically metal oxides) Auger can be extremely difficult. However, with careful sample preparation and appropriate Auger operating conditions, excellent data can still be obtained from these challenging materials.

In this investigation Auger elemental mapping and small area spectroscopy were used to study the changes that occur between fresh and aged Cs-promoted, alumina-supported Ag catalyst samples. The results show that while the size of the alumina support particles remains roughly the same during extended use, the Ag catalyst morphology has changed dramatically with the particle size increasing by over an order of magnitude. Conversely, the Cs Auger maps from the Fresh and Aged catalysts show that this constituent remains dispersed across the alumina support during the aging process.

**HC-ThP3 CO Adsorption on Size-selected $Pt_n$ Clusters Uniformly-Deposited on $Al_2O_3$/NiAl(110)**, ***Yoshihide Watanabe***, *A. Beniya,* Toyota Central R&D Labs. Inc., Japan

Size-selected metal clusters on oxide surfaces are a subject of considerable interest because of their distinctive size-dependent catalytic properties. The most precise approach to prepare a model catalyst is deposition of size-selected clusters using a mass-filtered cluster ion beam. It is important to prepare a uniformly deposited surface and avoid cluster-aggregations for investigation of size-dependent catalytic activity.

Pt clusters produced using a DC magnetron-sputtering source were mass-selected using a quadrupole mass filter. The parallel plate deflectors were placed to scan the cluster ion beam. When two sine voltage waveforms are applied to the orthogonal deflectors, the ion trajectory on the surface produces a Lissajous pattern. The ion trajectory fills the sample surface uniformly with an irrational frequency ratio. The advantages of this method are simplicity and low cost of setup compared with raster scanning method.

In this study, size-selected Pt clusters were deposited uniformly on surfaces by scanning the cluster ions in the form of Lissajous pattern. We confirmed that size-selected clusters can be deposited uniformly on a surface by Pt 4f intensity mapping. A uniform cluster distribution was also confirmed using a scanning tunneling microscope.

In high-density condition, the Pt clusters deposited without Lissajous scan could aggregate and form different size clusters. Cluster aggregation probability depends on the deposited density. The isolated $Pt_n$ clusters and their aggregates were estimated to be distributed with position-dependence. At 0.1 ML of total coverage, 33% of the clusters coalesce to form larger clusters. This result indicates that the coverage needs to be low enough to neglect the cluster aggregation effect.

The adsorption states of CO molecules on size-selected $Pt_n$ ($n$ = 7, 15, 20) clusters deposited on the $Al_2O_3$/NiAl(110) surface were also investigated with and without a Lissajous scan. Two peaks at 2020 and 2040 $cm^{-1}$ are observed in infrared reflection absorption spectroscopy (IRAS) spectra of adsorbed $^{13}CO$ at saturation coverage. These peaks are assigned to adsorbed CO at the on-top site of slightly cationic Pt atoms interacting with substrate oxygen atoms (2040 $cm^{-1}$), and of neutral Pt atoms bound by the Pt–Pt bond (2020 $cm^{-1}$). Temperature programed desorption (TPD) spectra of saturated $^{13}CO$ were also investigated. Combining the IRAS and TPD results, we determined that CO molecules bind to slightly cationic Pt atoms with an adsorption energy of 0.7–1.0 eV, and bind to neutral Pt atoms with an adsorption energy of 1.4 eV.

**HC-ThP4 Unexpected Formation of Catalytically Active Palladium Nanoparticles on Silica Surface in Organic Solvents**, ***Megan Bornstein***, *A. Quast, R. Park, J. Shumaker-Parry, I. Zharov*, University of Utah

Supported palladium nanoparticles (PdNPs) have been found to be active catalysts for a variety of organic transformations, with more recent reports showing PdNPs can catalyze chemoselective hydrogenation, as well as the photocatalytic activity of PdNPs can be enhanced plasmonically. Having a method to reliably synthesize small PdNPs on inorganic supports is useful, and we will report on the formation of PdNPs on silica nanospheres in organic solvents, which can be used as a convenient method of PdNPs preparation.

While attempting to immobilize $Pd^{2+}$ ions on ligand-modified silica nanospheres, we observed the formation of small (~5 nm) uniform PdNPs. The only reactants in this process were surface-functionalized silica spheres, $Pd(OAc)_2$, and reagent-grade acetone. This suggests that an impurity in the acetone is responsible for the reduction of $Pd^{2+}$ to $Pd^0$. We obtained similar PdNPs when using high purity acetone containing a small amount of added ethanol, while no PdNPs formation was observed in acetonitrile. Thus, this suggests that PdNPs is due to the presence of reducing organic compounds, such as alcohols.

The oxidation state of palladium was confirmed using X-ray photoelectron spectroscopy (XPS), and the morphology of the particles was analyzed using Scanning Transmission Electron Microscopy (STEM). The PdNPs formed were very small, typically around 5 nm in diameter when the reaction was done at room temperature, and uniformly distributed on the surface of a silica support that had been functionalized with primary amines or BiPy ligands, which provide stabilization for the PdNPs. For reactions run at 40 °C, the average diameter of the PdNPs was larger than those run at -77 °C or room temperature. The materials synthesized were capable of catalyzing the reduction of 4-nitrophenol to 4-aminophenol and the oxidation of benzyl alcohol to benzaldehyde.

**HC-ThP5 Copper Activated Conversion of Ethanol to Higher Alcohols over Hydrotalcite Derived MgAl Mixed Oxides**, ***Karthikeyan K. Ramasamy***, *M. Guo, M. Gray, S. Subramaniam*, Pacific Northwest National Laboratory, *A. Karakoti*, Ahmedabad University, India, *V. Murugesan, V. Shutthanandan, S. Thevuthasan*, Pacific Northwest National Laboratory

Unique physical and chemical properties of layered double hydroxide, hydrotalcite (HT) ($M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}A^{n-}x/n\cdot mH_2O$), derived materials have been used for selective and efficient transformations of organic compounds to higher value products. The catalytic properties of the HT derived mixed oxide material are a function of the morphology, local structure and oxidation state of the participating cations. In this work the effect of addition of copper ions on the catalytic properties of MgAl HT derived materials were studied for selective conversion of ethanol to higher alcohols. The ethanol to higher alcohol conversion goes thru a series of complex intermediate steps. The addition of copper is expected to promote the catalytic dehydrogenation of alcohols to aldehydes which is the first step in the complex cascade reaction and considered as the rate determining step in the overall chemistry. Various concentration of copper loading were attempted from 0 wt% to 6 wt % using different synthesis strategies in an attempt to achieve a homogenous dispersion of copper in the MgAl matrix. The selectivity and efficiency of copper substituted catalysts were analyzed by conversion of ethanol to higher alcohols in an indigenously designed plug flow reactor. Resulting physical and chemical changes in copper substituted catalysts were studied before and after the catalytic reaction using high resolution transmission electron microscopy, x-ray diffraction, x-ray absorption, X-ray photoelectron spectroscopy and nuclear magnetic resonance measurements. It was observed that different oxidation states of copper and the extent of dispersion of copper in the HT matrix influences catalytic efficiency and selectivity of the process by promoting various side reactions. Synthesis of copper substituted HT derived mixed oxide catalyst plays a major role in controlling the dispersion of the copper in the matrix. Fundamental challenges in achieving higher copper substitution without observing significant clustering and aggregation effects will be discussed in context of catalytic selectivity and efficiency.

**HC-ThP6 Methane Dissociation on Ni(111) at High Surface Temperatures: The Observed role of Surface and Subsurface C on Reactivity**, ***Eric Dombrowski***, *E. High, A.L. Utz*, Tufts University

Steam reforming methane over a Ni catalyst is the chief industrial process for $H_2$ gas production, and activation of methane's C-H bond to form surface-bound $CH_3$ and H is rate limiting. Conventional and vibrational state-selected molecular beam studies have highlighted the importance of translational ($E_{trans}$) and vibrational ($E_{vib}$) energy in promoting this rate limiting step on clean, well-ordered Ni single crystal surfaces. Nearly all of these studies have been performed at low to moderate surface temperatures ($T_{surf}$< 700K), where carbonaceous reaction products remain bound to the surface throughout the measurement.

Here, we describe experiments that extend these state-resolved measurements to the high surface temperatures typically used in the steam reforming process. Under these conditions,the methyl product promptly dehydrogenates to form surface-bound C and H, and H atoms recombinatively desorb, leaving C on the surface. The remaining carbon can dissolve into the nickel subsurface or bulk during the molecular beam dose, with a $T_{surf}$-dependent dissolution rate. We measured methane uptake onto, and into, a Ni(111) single crystal *in situ* across a range of surface temperatures from $T_{surf}$ = 680 – 850 K. We varied incident translational energies and incident methane flux, and measured S(θ) for both laser-off and state resolved (v=1, $v_3$ antisymmetric C-H stretch) methane. A unique molecular beam reflectivity method allowed us to quantify the initial $S_0$ as well as S(t) in real time during the dose. Integrating S(t) yielded the integrated amount of C deposited during the dose, (θ) and allowed us to calculate S(θ).

Over the $T_{surf}$ range studied, we observed drastic differences in carbon dissolution during deposition. At $T_{surf}$ = 680K, carbon uptake into the nickel lattice was minimal and about 0.5 ML of C was deposited before the surface became deactivated due to site-blocking. This situation changed dramatically at temperatures above $T_{surf}$ = 750 K. At intermediate temperatures, we observed an induction period prior to the onset of site blocking and surface passivation, and, at $T_{surf}$ = 850 K, deposition of more than 50 ML of C did not completely passivate the surface. Furthermore, we observed that under some conditions, S(θ) *increased* with increasing C concentration beneath the surface. A simple two-step dissolution process that includes T-dependent rate constants for C transport between the surface, subsurface, and bulk qualitatively describes our data. We will also describe our most recent efforts to refine this model to more quantitatively describe our experimental measurements to better understand the role of dissolved C on methane activation.

## Advanced Ion Microscopy Focus Topic
## Room: Central Hall - Session HI-ThP

## Advances in Ion Microscopy Poster Session

**HI-ThP1 Sub-10 nm Width High Aspect Ratio Trench Patterning of Gold Film using Helium Ion Microscope**, ***Etsuo Maeda***, The University of Tokyo, Japan, *T. Iijima*, National Institute of Advanced Industrial Science and Technology (AIST), Japan, *R. Kometani*, The University of Tokyo, Japan, *S. Migita, S. Ogawa*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

The helium ion microscope (HIM) realized the sub-nm level imaging with helium (He) ion beam from single tungsten atom on the top of the trimer. There are numbers of study focusing on nanostructure imaging, for example carbon nanotubes, graphene films, and self-assembled monofilms [1-3]. Through these previous studies, the advantages of HIM for imaging with high resolution and high contrast have been proved.

In our work, an HIM (Carl Zeiss ORION PLUS at AIST SCR station) was applied for sub-10 nm He ion beam etching to realize nano-gap trenches of high aspect ratio for the high sensitive surface enhanced Raman scattering (SERS) devices consisted by gold (Au) structures. To reveal the penetration depth of the He ions into the Au film with 30 kV acceleration voltage, two-body collision calculation was performed [4]. As the results of the calculation, the expected penetration depth was decided as 200 nm. Following the penetration depth results, Au films were prepared (70, 160, and 700-nm-thick) on 500-nm-thick silicon dioxide ($SiO_2$) layer. After a focused He ion beam irradiation ($10^{20}$ ions/$cm^2$, acceleration voltage: 30kV, beam current: 2.5 pA), a cross section shape was evaluated with Z-contrast transmission electron microscopic (TEM) images.

In case of thin films (70 and 160-nm-thick), funnel shapes from beam profile were observed. The dimension of the funnel shape was ~40 nm as width and ~35 nm as depth. The narrowest gap size was 5.5 nm for 70-nm-thick Au film and 1.4 nm for 160-nm-thick Au film. The lowest estimated aspect ratio of the nano-gap trench was 24.0 with 160-nm-tchik Au film. Moreover, observed Au atom penetration depth of 160-nm-thick Au film was 20% lager than that of 70-nm-thick Au film. With 70-nm-thick Au film, the fabricated narrow gap was destroyed by recoiled He ions from an interface between the Au film and $SiO_2$ layer.

Unlike the thin Au films, a thick Au film (700-nm-thick) showed blistered shape in the middle of the film as expected. The fissures in the thick Au film could be related to the blistering phenomena as seen in the Si substrate. He ions which could not path through thick Au film might be gasified in the thick Au film. For the purpose of realizing the nano-gap trenches for SERS devices, we need more structural and morphological characterization to suppress these blistering phenomena.

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**HI-ThP2 Optimized *ex situ* Lift Out of FIB Prepared Specimens**, ***Lucille Giannuzzi***, EXpressLO LLC

Focused ion beam (FIB) microscopes may be used to prepare site specific lift out specimens for subsequent characterization by transmission electron microscopy, surface science, or other analytical techniques [1-3]. *ex situ* lift out (EXLO) exploits the physics of adhesion forces for picking up a specimen with a solid probe tip and placing or manipulating it to a suitable carrier [1-3]. In this presentation, techniques for fast, easy, and successful lift out and manipulation reproducibility rates are described. Once the specimen is lifted out to the probe, the probe can be rotated to position the specimen either on top of, or under the probe, depending on the type of carrier to be used. In addition, since the specimen is not rigidly fixed to the probe, the specimen orientation can be rotated about the probe using the carrier itself, for precise positioning in just a couple of minutes. Precise orientation of the specimen with respect to the probe provides the greatest success rates, reliability, and throughput of the manipulation process. These and other methods will be fully described and presented.

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## Manufacturing Science and Technology Group
## Room: Central Hall - Session MS-ThP

## Topics in Manufacturing Science and Technology

**MS-ThP1 Influence of Strain Rate on Deformation Behaviour of an AX52 Alloy Prepared by ECAP**, ***Kristyna Halmesova***, Comtes Fht, Czech Republic, *Z. Trojanova*, Charles University, Prague, Czech Republic, *J. Dzugan*, Comtes Fht, Czech Republic, *P. Minarik*, Charles University, Prague, Czech Republic

Cast magnesium alloy AX52 (nominal composition Mg-5Al-2Ca in wt.%) was processed by equal channel angular pressing (ECAP) using A route and 1-8 passes. The microstructure and texture of samples have been assessed using electron backscatter diffraction and X-ray diffraction. The differences in grain size measured by these techniques allow for an understanding of microstructural evolution. Samples were tested in tension at room temperature initial strain rates in the interval from $1 \times 10^{-3}$ to $1 \times 10^{2}$ $s^{-1}$. The results reveal a significant strain rate sensitivity, which is affected by the ECAP processing. Deformation at higher strain rates became to be unstable. Deformation mechanisms operating at various strain rates are discussed in connection with microstructure and texture.

**MS-ThP4 Material Characterization of Tungsten Dispenser Cathodes**, ***Briana Fees***, San Jose State University and Coherent Inc

Barium impregnated tungsten dispenser cathodes are a critical component in the production of ion plasma lasers. As the emission source for the generation of plasma, the final processing, i.e. activation, of the cathode plays a crucial role in the emission of electrons as well as the lifetime of the laser. This activation process serves two primary purposes; the first being outgassing of impurities, adsorbed and absorbed during cathode processing and atmospheric exposure; the second being conversion of the impregnated barium oxide into free barium on the surface of the cathode, as the barium is the actual ion source. The objective of this work is to perform a full characterization of key process indicators which most influence activation. Preliminary results show a large variance in the resistance of cathode lots indicating a need for unique processing.

## Nanometer-scale Science and Technology Division
## Room: Central Hall - Session NS-ThP

## Nanometer-scale Science and Technology Poster Session

**NS-ThP1 Co-deposition of Nanoparticle – Diamond-Like Carbon Composite Thin Films**, ***Ajai Iyer***, *J. Etula, N. Wester, J. Koskinen*, Aalto University, School of Chemical Engineering, Finland

Nanoparticles have been proven to have properties very different from bulk materials and extensive research is undertaken to ascertain application based nanoparticle functional properties. One of the most elegant solutions for nanoparticle usage is to form a composite thin film with desired nanoparticles embedded in a matrix. Such composite films are generally fabricated in one of two ways. Either the nanoparticles are synthesized in-situ during the film growth process or the nanoparticles are seeded prior to film growth process. We propose a unique method of using physical vapour deposition methods to co-deposit pre-processed nanoparticles in tandem with the matrix material forming a composite thin film. These composite films could be deposited as single or multi-layer bulk films or as films with nanoparticle concentration gradient throughout the film thickness. The matrix material is chosen to be diamond-like carbon (DLC) with controllable $sp^3$ to $sp^2$ bonded carbon ratio, allowing the film to have a wide range of mechanical, optical and electrical properties. Co-deposition of nanoparticles with DLC results in composite films where nanoparticles are embedded into a DLC matrix. The effect of the type and concentration of nanoparticles on the mechanical, optical and electrical properties of the composite film are currently under study with possible application fields related to sensors, electrically conductive coatings, thin film optical waveguides and energy storage. In this work we demonstrate detonation nanodiamonds (DNDs) co-deposited with high quality DLC using a pulsed filtered cathodic vacuum arc (p-FCVA) method to form DND-DLC composite film. Transmission electron microscopy (TEM) has been used to verify the presence of DND agglomerates (sized few tens of nm) in the composite film as well as the crystallinity of the embedded DND nanoparticles. The DND nanoparticle concentration has been estimated to be of the order of 0.1 vol% in the composite film. The DND-DLC composite film has been measured to have around 16% enhancement in hardness and 40% reduction in wear in comparison to DLC film. Preliminary tests indicate that the composite film has potential as an electrochemical sensor and further tests are in progress. Results of co-deposition of other nanoparticles with DLC to form composite film are also discussed.

**NS-ThP2 Atmospheric Pressure Plasma Functionalization of Diamond Particles**, ***Gary McGuire***, *O.A. Shenderova, N.J. Nunn*, Adamas Nanotechnologies, Inc.

Dielectric barrier discharges are non-equilibrium plasmas which may operate at atmospheric-pressure avoiding the necessity of generating vacuum conditions. Operation at atmospheric pressure facilitates the introduction and surface functionalization of gram quantities of nanoparticles within minutes at room temperature as an alternative means to high temperature processes which typically takes hours. In this study nanodiamond particles of detonation origin were fluorinated using $CF_4$. Surface analysis using x-ray photoelectron spectroscopy confirmed a fluorine concentration of up to ~4.5 at% of the nanodiamond particles surface. Fourier transform infrared spectroscopy revealed the presence of F-bands, related to $CF_3$ - ($CF_2$) stretching vibrations and symmetric and asymmetric $CF_2$ vibrations. Fluorine surface functional groups can serve as a means for further chemical substitution reactions so that other, more complex functional groups such as amino acids, oligonucleotides, peptides, etc. can bond to the surface, facilitating material applications for biosensors. It has been demonstrated that an atmospheric pressure dielectric barrier glow discharge is a highly effective means to rapidly fluorinate, oxidize and aminate diamond surfaces.

**NS-ThP3 Nanometer-scale Etch Characteristics of TiN Thin Films using Inductively Coupled Plasma of $Cl_2/C_2F_6/Ar$**, ***JaeSang Choi***, *J.Y. Lee, D.H. Cho, C.W. Chung*, Inha university, Republic of Korea

As the information era has come, high performance semiconductor memory devices which have the characteristics containing high density, fast process time, lower power consumption for faster mass data transfer has been required. To satisfy these demands, scaling down to nanometer scale for etching process has been important in fabricating semiconductor devices. Titanium nitride (TiN) thin film has been widely employed as a hard mask due to its fine property such as good thermal and chemical stability, and good adhesion than conventional inorganic masks. In the past, there were some studies on TiN films using $Cl_2$, $BCl_3$, $NF_3$, $CF_4$, and $SF_6$ gases [1-3]. However, the etching process of nanometer-sized TiN films was rarely investigated.

In this study, nanometer-scaled e-beam resists were patterned on TiN thin films and inductively coupled plasma reactive ion etching using $Cl_2/C_2F_6/Ar$ gas mixtures was applied to investigate the characteristics of TiN thin films. First, a variety of gas ratio was examined to find out best etch profile using micro-patterned TiN thin films. Then, based on these results, the nanometer-patterned TiN thin films using $Cl_2/C_2F_6/Ar$ gas mixtures were investigate in terms of etch selectivity and etch profile. Finally, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy will be performed on the etched TiN films to elucidate the etch mechanism.

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### NS-ThP4 Etch Characteristics of Magnetic Tunnel Junction Stacks using Pulse-modulated RF Source Plasma

***JaeYong Lee***, *J.S. Choi, D.H. Cho, C.W. Chung*, Inha University, Republic of Korea

The source/bias pulse-time modulated RF plasma has been introduced to progress further in convoluted challenges from conventional continuous wave (CW) plasma such as fatal etch damage, low etch selectivity, and etch residues. This modulated plasma means the plasma condition modified by a specific matching system which can change on-off duty ratio of 13.56MHz RF power and frequency on the specific duty ratio. Especially, since the magnetic materials used for magnetic random access memory (MRAM), which is a promising candidate for next generation semiconductor, have less reaction with even corrosive gases, this process can offer a prospective approach. Some researches on etch characteristics of magnetic materials using bias-pulse time modulated plasma has been reported, resulting in improved etch profiles compared to CW plasma . However, few studies on the magnetic materials using source-pulsed plasma can be found.

In this study, etch characteristics of nanometer-scale patterned magnetic tunnel junction stacks (MTJs), which is a critical component of MRAM, using the pulsed modulated RF source plasma were investigated. The MTJs consisted of TiN/Ta/CoFeB/MgO/CoFeB/Ta on the $SiO_2$ substrate and E-beam resists of 70×70 $nm^2$ were patterned on the TiN hardmasked MTJ stacks. In the plasma process, the non-corrosive gas mixture of $CH_4/O_2/Ar$ was used. The effects of on-off duty ratio and frequency of pulsed plasma on the etch characteristics of MTJ stacks were examined.

### NS-ThP5 Dry Etching of Nanometer-scale Patterned CoFeB Thin Films under Pulse Modulated Plasma

***DooHyeon Cho***, *J.S. Choi, J.Y. Lee, C.W. Chung*, Inha University, Republic of Korea

Dynamic random access memory device has been commercially sucessful. However this device has disadvantages such as volatility and scaling problem. Spin transfer torque magnetic random access memory(STT-MRAM) has been recieved a great attention as the next-generation memory device owing to the advantages such as non-volatility, high density, unlimited endurance and low operating voltage[1]. The STT-MRAM devices are composed of magnetic tunnel junction stacks (MTJs) and CMOS. As the dimension of MTJs is decreased, perpendicular magnetic anisotropy (PMA) is necessary for high density MRAM. Therefore, the MTJs comprised of multilayers incluing CoFeB thin films should be fabricated in nanometer-scale dimension for PMA [2]. In order to realize this demand for high density MRAMs, the magnetic thin films such as CoFeB, CoPt, PtMn and so on should be patterned in nanometer-scale.

In the previous studies, micrometer-scale patterned CoFeB thin films showed relatively good etch profiles using $CH_3OH$, $CH_3COOH$ and $CH_4/O_2/Ar$ [3,4,5]. In this study, the etch characteristics of nanometer-scale patterned CoFeB thin films using $CH_4/O_2/Ar$ gas mixture under pulse-modulated plasma were investigated. The main parameters in pulsed-modulated plasma, which are on-off duty ratio and pulse frequency, were applied to investigate the etch characterisitic of CoFeB thin films. Finally, high degree of anisotropy of the etched CoFeB films with 70 x 70 $nm^2$ patterns were obtained and the etch mechanism also was examined using optical emission spectroscopy, X-ray photoelectron spectroscopy and TEM micrographs.

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### NS-ThP6 The Formation of Stable $GeO_2$ Oxide using the High Pressure Oxidation

***Juhyun Bae***, *I.S. Chung*, Sungkyunkwan University, Republic of Korea

Thermal oxidation of Ge has been investigated under high pressure ambient to suppress GeO vaporization. Ge oxide was grown in the temperature range of 450 °C to 550 °C in dry $O_2$ ambience at three different pressures such 10, 30, and 50 atm. The physical property of $GeO_2$ is analyzed using the transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Additionally, C-V characteristics were obtained from $GeO_2$/Ge MOS capacitors. The hysteresis in C-V characteristics and the interface trap density ($D_{it}$) are significantly reduced as the pressure increases. Consequently, the properties of both $GeO_2$ film and $GeO_2$/Ge interface are successfully improved by suppressing GeO volatilization utilizing high pressure.

### NS-ThP8 Controlling Kondo Resonances of Magnetic Molecules on Au(111) by Binding of Metal Atoms

***MinHui Chang***, Korea University, Republic of Korea, *Y.H. Chang*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea, *H. Kim, S.H. Lee*, Korea University, Republic of Korea, *Y.H. Kim*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea, *S.-J. Kahng*, Korea University, Republic of Korea

Controlling and sensing spin states of magnetic molecules at the single molecule level is essential for spintronic molecular device applications. The exchange coupling between magnetic-molecules and metallic substrates has been actively studied by measuring Kondo resonances at Fermi level. The resonances have been controlled by small molecule bindings, but not by adsorption of metal atoms to magnetic-molecules. Here, we demonstrate that Kondo resonances of Co-porphyrin on Au(111) can be controlled by adsorption of metal atoms, and be sensed using scanning tunneling microscopy and spectroscopy (STM and STS). Bare Co-porphyrin showed a clear zero-bias peak, a signature of Kondo resonances in STS, whereas Co-porphyrin adsorbed metal atoms showed modified zero-bias resonances, with reduced full width half maximum or Kondo temperature. Our density functional theory calculation results explain it with spatial redistribution of unpaired spins in d-orbitals of Co-porphyrin by the adsorption of metal atoms. Our study shows that the spin-state of metallo-porphyrin can be modified in multiple ways by the adsorption of additional metal atoms, and be probed through Kondo resonances with STS.

### NS-ThP9 Nanolithography Toolbox: Design Solutions for Nanoscale Devices

***Roberto De Alba***, *K.C. Balram, D.A. Westly, M. Davanco, K.E. Grutter, Q. Li*, NIST, *T. Michels*, GenISys GmbH, *C.H. Ray, L. Yu, R.J. Kasica, C.B. Wallin*, NIST, *D.A. Czaplewski, L.E. Ocola*, Argonne National Laboratory, *S. Krylov*, Tel Aviv University, Israel, *P. Neuzil*, Brno University of Technology, Czech Republic, *K. Srinivasan, S.M. Stavis, V.A. Aksyuk, J.A. Liddle, B.R. Ilic*, NIST

Various lithography patterning technologies can be used to define structures with nanometer-scale lateral dimensions. The first step in any lithographic process consists of device design. There are a number of available design packages that output semiconductor-standard graphic database system (GDSII) files, which is a binary format representing planar geometric shapes. The predominance of IC devices in manufacturing has led to the development of software packages that are ideal for designing and laying out integrated circuits, which typically have rectilinear geometries, where shape edges are parallel to the *x* and *y* axes. Consequently, many of these software packages are not ideal for designing curved geometries with aggressively-scaled dimensions for nanophotonic, nanoplasmonic, nanofluidic, and nanomechanical devices. To solve this design problem, we have developed a computer-aided design (CAD) software package for streaming complex shapes to GDSII. The platform-independent Nanolithography Toolbox runs on Linux, Windows and MacOS, and is free for users to download from the Center for Nanoscale Science and Technology at the National Institute of Standards and Technology (CNST) website ( http://www.nist.gov/cnst/ ).

The CNST developed the Toolbox to help users of the CNST NanoFab to design their nanoscale devices, particularly those with curved features and small dimensions. The Toolbox offers design features that are difficult to implement in software optimized for IC design, and allows users to rapidly customize nanoscale shapes of arbitrary complexity. The Nanolithography Toolbox offers hundreds of parameterized shapes that are useful in a variety of applications spanning nanoscale photonics, mechanics, fluidics, electronics, and other disparate fields of scientific endeavor. Furthermore, the

Toolbox allows users to precisely define the number of vertices for each shape or to create vectorized shapes using Bezier curves. In the former case, the Toolbox constructs the resulting shapes with a uniform vertex distribution along the periphery, rendering symmetric objects. A shape-rendering parameter controls the number of vertices for vectorized objects. The parameter is set globally for all shapes, or individually for each shape. In the latter case, the resulting rendered shapes have an increased vertex density at higher curvatures. A full description of the all the capabilities of the Toolbox can be found in the manual.

**NS-ThP10 Visualizing Silicide Formation via Interface Electrostatics with BEEM**, ***Westly Nolting***, SUNY Polytechnic Institute, *C. Durcan*, SUNY College of Nanoscale Science and Engineering, *V. LaBella*, SUNY Polytechnic Institute

Nanoscale fluctuations in the electrostatics of a metal semiconductor interface impact performance and are important to understand and measure, which can be accomplished with ballistic electron emission microscopy (BEEM), an STM based technique. In this work, we perform BEEM on Cr/Si Schottky contacts to visualize the interface electrostatics to nanoscale dimensions to understand the effects of silicide formation. This is accomplished by acquiring tens of thousands of spectra on a regularly spaced grid and fitting the results to determine the local Schottky barrier height. Monte-Carlo modeling is utilized to calculate the barrier height distributions that includes scattering of the electrons that traverse the metal layer and a distribution of electrostatic barriers at the interface. Improved agreement between the model and the data is achieved when specifying more than one barrier height, providing a signature of silicide formation. This, and recent work extended this method to the W/Si interface will be presented.

**NS-ThP11 Dimensionality Effects in $FeGe_2$ Nanowires: Enhanced Anisotropic Magnetization and Anomalous Electrical Transport**, ***Ivan Kravchenko***, Oak Ridge National Laboratory, *S. Tang*, Central South University, PR China, *T.Z. Ward, Q. Zou*, Oak Ridge National Laboratory, *J. Yi*, University of Tennessee, *C. Ma, M. Chi, G. Cao, A.-P. Li, D.G. Mandrus, Z. Gai*, Oak Ridge National Laboratory

We report the synthesis of single-crystal iron germanium nanowires via chemical vapor deposition without the assistance of any catalysts. The assembly of single-crystal $FeGe_2$ nanowires with tetragonal C16 crystal structure shows anisotropic magnetic behavior which is ferromagnetically coupled perpendicular to the wires and antiferromagnetically coupled parallel to the wires' long axis. Single $FeGe_2$ nanowire devices were fabricated using e-beam lithography. Transport in these devices show two resistivity anomalies near 250 K and 200 K which are likely signatures of the two spin density wave states in $FeGe_2$.

**NS-ThP12 A High Coherence Package for Quantum Circuits Containing Topologically Isolated Qubits**, ***Vivekananda Adiga***, *N.T. Bronn, S.B. Olivadese*, IBM Research Division, T.J. Watson Research Center, *X. Wu, D.P. Pappas*, NIST Boulder, *J.M. Chow*, IBM Research Division, T.J. Watson Research Center

We demonstrate a package containing a superconducting quantum processor wherein we use Pogo pins (50 Ohm) to access the topologically isolated qubits. This allows us to enclose our quantum processor in a non-magnetic environment where we can maintain RF-Hygiene and the entire assembly is compatible with low temperature operation. Self-alignment of the parts allows for rapid testing and scalable integration. We demonstrate low energy loss and high phase coherence comparable to the standard packages involving wirebonds. Single and two-qubit gate fidelities are on par with standard packaging schemes with cross talk less than -40 db at the frequencies of operation. Results are promising for integration with extensible qubit architectures.

**NS-ThP16 Few-Wall Carbon Nanotube Coils**, ***Dekel Nakar***, *R. Popovitz-Biro, K. Rechav, E. Joselevich*, Weizmann Institute of Science, Israel

Various electronic components based on carbon nanotubes (CNTs) have been produced, but an induction coil has not been demonstrated yet. Our group previously created defect-free single-wall CNT coils, but short-circuiting between turns prevents the coils from acting as inductors. To overcome this limitation, here we explore the use of few-wall CNTs, in which the outer walls may act as sheathing for the inner walls. We show the successful formation of the first few-wall CNT coils from individual CNTs and thin bundles.We characterized the structural properties of the coils using optical microscopy, SEM, AFM, top-view TEM and cross-sectional TEM. We also characterized their electrical properties. The coils comprised CNTs of two, three and four walls without observable defects. The coils had up to 163 turns and diameters between 1 and 5 µm. Based on the structural results, we suggest a mechanism for the formation of the coils. These ordered coils extend the known repertoire of self-organized structures of 1D nanomaterials. They are also promising candidates for inductive devices, and for manifesting other interesting properties, such as electromagnetism and superconductivity.

Nakar, D.; Popovitz-Biro, R.; Rechav, K.; Joselevich, E., "Few-Wall Carbon Nanotube Coils", *in preparation*.

## Advanced Surface Engineering Division
## Room: Central Hall - Session SE-ThP

## Advanced Surface Engineering Poster Session

**SE-ThP1 Surface Passivation of Energetic Particles Via Atomic Layer Deposition**, ***Kai Qu***, Huazhong University of Science an Technology, PR China, *C.L. Duan, P.H. Zhu, J.M. Cai, R. Chen*, Huazhong University of Science and Technology, PR China

Energetic particles, such as aluminum hydride ($AlH_3$) and aluminum (Al) nanoparticles, have shown great potentials for military and astronautic uses. Due to their high reactivity, the practical implementations of these materials rely on their safe storage, handling, transportation, etc. For example, during the storage of $AlH_3$, hydrogen could be slowly released through reaction with moisture and oxygen. When mixing $AlH_3$ with other fuels or transportation, the heat generated from inter-particle friction may lead to the temperature rise, resulting in rapid hydrogen release and may trigger explosion. When fabricate explosive in water at 60-70°C, aluminum nanoparticles will react with water molecules. Thus it is imperative to passivate the $AlH_3$ and Al particles to improve their stabilities. In this talk, both $\alpha$-$AlH_3$ and Al particles were passivated *via* atomic layer deposition to improve their storage, transportation, and mixture stabilities. The transmission electron microscopy showed conformal amorphous $Al_2O_3$ shells around the crystalline $AlH_3$ cores. The hydrogen capacity was well retained after hydrothermal aging test. The friction sensitivity got reduced, while the overall hydrogen capacity and dehydrogenation speed are kept about the same. For Al nanoparticles, a few cycles of compact ALD coating could completely isolated the water bath at 60°C-80°C. The minimum thickness of coating layers ensured that high energy of the Al nanoparticles were well retained.

## Thin Films Division
## Room: Central Hall - Session TF-ThP

## Thin Films Poster Session

**TF-ThP1 Hydrogen Bond Mediated Supramolecular Self-Assembly To Direct Thin Film Morphology For Organic Electronic Applications**, ***Daken Starkenburg***, University of Florida

Phthalhydrazide, barbiturate, guanine, and diaminotriazine hydrogen bonding units have been integrated into pi-conjuagated oligomers. The addition of hydrogen bonding units on to one or both ends of the oligomers may be used to guide their self-assembly into optimized 2D and 3D morphologies for efficient charge separation and extraction in OPV devices. Scanning tunneling microscopy revealed several possible 2D ordered structures for vacuum deposited ditopic oligomers with diaminotriazine units dependent on processing conditions. Methyl and octyl chains were also added to the hydrogen bonding oligomers which led to easier film processing and the capability for designed modifications of the 2D structure. Furthermore, previously reported small molecules are currently being modified to integrate hydrogen bonding into a monotopic design in an effort to optimize 3D morphology and demonstrate high power conversion efficiencies for organic solar cells.

**TF-ThP5 Indium Doped ZnO Nanopowders Synthesized by MW-HTS and their Physical Characterization**, ***Mujdat Caglar***, Anadolu University, Turkey, *K. Gorgun*, Eskisehir Osmangazi University, Turkey, *S. Aksoy*, Sinop University, Turkey, *S. Ilican, Y. Caglar*, Anadolu University, Turkey

Zinc oxide (ZnO) are currently of great importance mainly as, transparent conductive electrodes, in solar cells devices, inorganic light emitting diodes, such as UV light emitting diodes, UV lasers and blue luminescent devices, photodetectors, gas sensors etc. The microwave synthesis is a synthesis method which is entirely different from the other methods. In the microwave method, a microwave diffuses to the material being heated volumetrically. In this study, Indium (In) doped ZnO nanopowders were synthesized via microwave assisted hydrothermal synthesis (MW-HTS) using zinc acetate dihydrate, indium acetate hydrate and sodium hydroxide. The effect of In dopant on the structural and morphological properties of ZnO nanopowders was investigated. To investigate the crystalline structure and the orientation of the doped ZnO nanopowders, XRD patterns were used. The lattice parameters and texture coefficient values of these nanopowders were determined. Field emission scanning electron microscope (FESEM) was used to analyze the surface morphology of the In doped ZnO. The presence of functional groups and the chemical bonding due to In doping are confirmed by Fourier transform infrared spectra (FTIR). **Acknowledgements:** This work was supported by Anadolu University Commission of Scientific Research Projects under Grant No. 1402F055 and 1705F259.

**TF-ThP6 Effect of Erbium on the Structural and Morphological Properties of ZnO Films by MW-CBD and its Application in Heterojunction**, ***Yasemin Caglar***, Anadolu University, Turkey, *K. Gorgun*, Eskisehir Osmangazi University, Turkey, *S. Aksoy*, Sinop University, Turkey, *M. Caglar, S. Ilican*, Anadolu University, Turkey

The doped zinc oxide (ZnO) films have attracted much attention because of their great potential for application to transparent conducting electrodes and insulating or ferroelectric layers in optoelectronic devices. Since ZnO has a wide bandgap energy of 3.37 eV at room temperature, its nanocrystals are suitable host materials for doping elements such as rare-earth (RE) and transition metal (TM) ions which are optically and magnetically active. RE doped ZnO nanocrystals are a potential candidate material for flat panel display phosphors due to efficient emission in the visible range, and different activators can be used to modify the color of luminescence. In this study, Erbium (Er) doped ZnO (ZnO:Er) films were deposited by microwave-assisted chemical bath deposition (MW-CBD). The structural and morphological properties of the films were investigated. Zinc nitrate hexahydrate was used as starting materials. The dopant source is Erbium (III) nitrat pentahydrate. The crystal structure and orientation of the films were investigated by X-ray diffraction (XRD) method. The films have the polycrystalline structure. Surface morphology of the films was also investigated by a scanning electron microscope (SEM). The *p-Si/n-ZnO:Er* heterojunctions were fabricated and their electrical properties were carried out in dark at room temperature. They were exhibited rectifying behavior by using thermionic emission theory. The important junction parameters such as ideality factor, barrier height and series resistance were systematically analyzed by the current-voltage (*I-V*) curves. **Acknowledgements:** This work was supported by Anadolu University Commission of Scientific Research Projects under Grant No. 1402F055 and 1705F283.

**TF-ThP7 Influence of Fluorine Incorporation on Structural and Optical Properties of ZnS Films**, ***Tulay Hurma***, Anadolu University, Turkey

ZnS has a wider band gap than other conventional II–VI semiconductors. Fluorine has a smaller atomic radius than both sulfide and zinc. ZnS and fluorine doped ZnS films were produced my means of ultrasonic spray pyrolysis (USP) method by spraying on glass substrates heated up to 340±5 °C. XRD and Raman spectroscopy were used to determine the crystalline formation and phase contents of these films and investigated the effect of fluorine having smaller atomic radius on both the structural and optical properties of the ZnS film. In addition to Raman spectroscopy, FTIR spectroscopy was used to detect the vibrations of atoms in the molecule. In the scope of morphological properties, SEM analysis was used and these images showed that the incorporation of fluorine in ZnS lattice caused important effects on the surface morphology and particle size. Optical absorption and reflectance spectra of the films that taken between 200 and 900 nm wavelengths were used to calculate the extinction coefficient, refractive index, dielectric constant and average refractive index values. The optical band gap and Urbach energy values of these films were determined depending on the fluorine incorporation.

**TF-ThP8 $WO_3$/Ag Electrochromic Multilayer Film by RF Magnetron Sputtering**, ***Chao-Te Lee***, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China, *P.K. Chiu, D. Chiang*, Instrument Technology Research Center, National Applied Research Laboratories, *W.-C. Chen*, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China, *J.-H. Xie, C.-C. Jaing*, Department of Optoelectronic System Engineering, Minghsin University of Science and Technology

In this work, the novel electrochromic $WO_3$/Ag multilayer film on ITO glass were designed and made by RF magnetron sputtering at room temperature. The effects of Ag film on the microstructure and optical properties of the $WO_3$/Ag multilayers were examined by field emission scanning electron microscopy, X-ray diffraction (XRD) and spectrometer. The average transmittance in the range from 400 to 700 nm of $WO_3$/Ag multilayer films was slight increased from 81.13 ($WO_3$/ITO glass) to 84.74%. The electrochromic characteristics of $WO_3$/Ag multilayer films were investigated by the bleaching and colored $WO_3$/Ag multilayer film. The variation of average transmittance in the visible range of bleaching and colored $WO_3$/Ag multilayer film is above 65%. Particularly, the average transmittance in the range from 800 to 1000 nm of $WO_3$/Ag multilayer film was greatly decreased from 74.21($WO_3$/ITO glass) to 1.59%. We found that novel $WO_3$/Ag multilayer film is suitable or electrochromic and hot mirror application.

**TF-ThP9 Crystalline Quality and Surface Roughness Optimization of Hetero-Epitaxial Titanium Nitride on Sapphire**, ***Hadley Smith***, University of Dayton, *A.N. Reed*, Air Force Research Laboratory, *S. Elhamri*, University of Dayton, *B.M. Howe, L. Grazulis, M.J. Hill*, Air Force Research Laboratory

In this project we optimized the growth of hetero-epitaxial titanium nitride (TiN) on sapphire using controllably unbalanced reactive magnetron sputtering. TiN is a mechanically-robust, high-temperature stable metallic material; these properties make TiN a material of interest for robust electrodes and resilient plasmonics. We adjusted deposition parameters such as external coil current, temperature, growth time and magnetron power to optimize the crystalline quality and surface morphology of TiN. Post-growth, we measured crystallinity using X-ray diffraction, and surface morphology using atomic force microscopy. X-ray diffraction showed a single TiN peak with pendellösung fringes; from these fringes we obtained a film thickness of ~55 nm. Atomic force microscopy showed a surface roughness of ~111 pm. Based on this characterization, we determined that the deposition parameters outlined in this presentation yielded (111)-oriented hetero-epitaxial TiN with minimal surface roughness. This optimization is a crucial first step in maximizing the usefulness of TiN for plasmonic applications.

**TF-ThP11 Water Repellency or Hydrophilicity of the PTFE Irradiated by an $Ar^+$Ion Beam**, ***Yuki Yamashita***, *I. Takano*, Kogakuin University, Japan

Recently, the application of polytetrafluoroethylene (PTFE) has spread to various fields. PTFE is a macromolecular material that has repetition of two fluorine atoms combined to a carbon atom. Because these atoms are strongly combined, PTFE has various excellent characteristics such as heat-resistant, chemical stability, low friction, etc. The significant characteristic among them is the high water-repellency which is well known as the coating of a cookware. The improvement of the water-repellency or hydrophilicity has been carried out by using the ion beam or the plasma treatment. In the case of the ion beam, the both properties of PTFE are able to be controlled by suitable ion beam energy.

Higher water-repellency of PTFE is required in a field such as a medical equipment, while higher hydrophilicity is anticipated to adhere between PTFE and the different material. Improvement of water-repellency and hydrophilicity are caused by the physical change of the surface morphology and by the chemical change of the molecular structure respectively.

In this study, the PTFE substrates of two types were used. Those are the adhesive tape type with 0.1mm in a thickness (T-PTFE: Chukoh Chemical Industries, Ltd.) and the sheet type with 1mm in a thickness (N-PTFE: NICHIAS Co.). Water-repellency or hydrophilicity of PTFE irradiated by an $Ar^+$ ion beam was investigated by the θ/2 method. The irradiated ion species were $Ar^+$ ions with 10kV in an acceleration voltage at 40 $\mu A/cm^2$ in a current density. Dependence of the PTFE substrate temperature was investigated at a range from -50 to 50 degrees using the control system of the liquid nitrogen cooling and the heater heating. Dependence of the irradiation time was changed from 0 s to 30 s in a room temperature. The surface morphology was observed by the laser microscope (OLS4500: Shimadzu Co.) and the SEM (JSM5310: JEOL Ltd.). The surface chemical state was measured using an X-ray photoelectron spectrometer (ESCA-K1s: Shimadzu Co.) .

In the case of the T-PTFE temperature dependence, the surface morphology changed hardly at -50 degrees, while the needle-like structure was clearly observed in the substrate temperature of 50 degrees. It was considered that the surface morphology was strongly influenced by the substrate temperature than by sputtering of the ion beam. From the XPS measurement, it was confirmed that F atoms were selectively sputtered at -50 degrees as showing the low contact angle, while the low contact angle was showed in the lower irradiation time of T-PTFE. It was considered that water-repellency and hydrophilicity of PTFE were influenced by the PTFE substrate temperature during the ion beam irradiation.

**TF-ThP12 Optical Chemical Sensors for the Detection of Taggants in Explosives**, ***Sarka Havlova***, *P. Fitl, M. Vrnata, E. Maresova, J. Vlcek, D. Tomecek, J. Herbst*, University of Chemistry and Technology Prague, Czech Republic

In this work, we present optical gas sensors with thin film of polymer as an active layer for the detection of taggants in explosives. The thin films of polymeric active layers based on poly(methyl methacrylate) (PMMA), polystyrene (PS) and low density polyethylene (LDPE) were prepared on lapped silicon substrates by spin coating with thicknesses in a range of hundreds nanometers (100 - 500 nm). These films were exposed to taggants' vapors such as 2-nitrotoluene (2-NT), 4-nitrotoluene (4-NT) and 2,3-dimethyl-2,3-dinitrobutane (DMNB) and measured in a range of their concentration 1 - 1000 ppm. Changes of refractive index were observed compared to reference atmosphere - synthetic air. The change of refractive index and layer thickness appears due to a swelling of the polymeric film in present of analyte vapors.

Thin films of polymers were subsequently doped with organic luminescent agents (metal phthalocyanines) and inorganic nanoparticles of rare earths (holmium oxide) and prepared with similar thicknesses. Soluble sulphonated metal phthalocyanines were dissolved and mixed with polymer solution, thin films were then prepared by spin coating. Insoluble phthalocyanines were evaporated under high vacuum conditions on the top of polymeric layer and localized laser melting of polymer was used for submerging of phthalocyanine molecules into the polymer matrix. These luminescent films were also exposed to vapors of taggants and changes in UV-VIS absorption spectra and luminescence spectra were detected. The influence of toluene was also evaluated for a comparison of detection properties with a substance similar to selected taggants.

The results suggest that gas sensors with these sensitive layers and based on connected optical techniques such as a measurement of luminescence, absorption and refractive index are very promising for the detection of taggants in explosives.

**TF-ThP13 The Effect of e-gun Deposition Process Variables on the Film Characteristics of the Chromium Oxide**, ***Po-Kai Chiu***, National Applied Research Laboratories, Taiwan, Republic of China, *Y.T. Liao, H.Y. Tasi*, National Tsing Hua University, Taiwan, Republic of China, *D. Chiang*, National Applied Research Laboratories, Taiwan, Republic of China

The film characteristics and optical properties of the CrOx films prepared by the e-gun deposition with the different process variables are investigated. The process variables include the various oxygen flow rates, applied substrate temperatures to 200°C, and with or without Ar and $O_2$ ion-assisted deposition. The optical constants of the deposited films with different process variables are determined from the reflectance and transmittance measurements obtained using spectrophotometer ranged from 350 nm to 2000 nm. The microstructures of the films are examined by the XRD, SEM, and XPS. The electrical conductivity is measured by four-point probe instrument. All the prepared films are amorphous without the significant pillar structure. The optical and electrical properties are illustrated by the analyzed XPS results with the ratio of the contribution of the free electrons to ion bonds in the deposited CrOx films. The major process variable to possess high extinction coefficient and low reflectance is the oxygen flow rate during the CrOx film deposition without ion-assisted deposition in the study.

**TF-ThP14 Fabrication of High-period-number Resonant Transition Radiation Emitters for Generation of Femto-second Hard X-rays**, ***Polly Wang***, National Tsing-Hua University, Taiwan, Republic of China, *C.T. Lee*, National Applied Research Laboratories, Taiwan, Republic of China, *A.P. Lee*, National Synchrotron Radiation Research Center, Taiwan, Republic of China, *K.C. Leou*, National Tsing-Hua University, Taiwan, Republic of China, *W.K. Lau*, National Synchrotron Radiation Research Center, Taiwan, Republic of China

Femtosecond resonant transition radiation (RTR) in x-ray region can be generated from alternatingly stacked multilayer structures when they are driven by relativistic ultrashort electron beams. In contrast to large-scale facility like x-ray free electron lasers (XFELs), compact x-ray sources of moderate peak brightness can be developed by using this method for some ultrafast scientific research. These structures can be fabricated by coating layer pairs of high and low density materials. Narrow-bandwidth x-rays can be generated by increasing the number of periods (i.e. the number of layer pairs). Thanks to the high transmittance of hard x-ray in most materials, the radiation bandwidth is not limited by x-ray absorption up to dozens or even hundreds of layers. In this report, we present our efforts on the development of a femtosecond narrow-band 12 keV x-ray source by driving high-period-number RTR emitters with the NSRRC photoinjector linac system which is operating in short bunch mode. Since the optimum thickness for one emitter period is of several hundred nanometers, total thickness of an emitter can be as thick as few tens of µm. Sputtering is considered as an appropriate process to fabricate these structures with reliable quality in reasonable time. The fabrication process of making such emitters that are composed of Mo/Si multilayers is under test. Structures of 60 periods (120 layers) have been fabricated. The estimated photon yield is about $3x10^4$ for a 100 pC drive beam. A portion of x-ray generated from multi-layer structure would be absorbed by the Si substrate of the emitter, so removing the substrate would be helpful to enhance photon flux. The process to remove the substrate is also discussed.

**Acknowledgement**

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**TF-ThP16 Materials and Methods for Bottom-Up Semiconductor Device Manufacturing by Selective Surface Modification**, ***Reuben Chacko***, *J. Lowes, J. Dai, S. Brown, D. Sweat*, Brewer Science, Inc.

In order to extend Moore's Law, device makers are looking at bottom-up approaches as an alternative for semiconductor device manufacturing. Recently, the variation in photoresist component distribution that is seen when scaling to sub-20-nm features has highlighted the need for very controlled and uniform distribution of materials. Bottom-up approaches to lithography patterning are able to address these stochastic issues, along with also addressing pattern roughness, excessive lithography steps, and others. We present novel materials and processes that enable selective surface modification with semiconductor device manufacturing as the end application. These materials are able to selectively deposit on various substrates, such as oxide, nitrides, metals, or even organic films. Properties such as selective deposition, catalysis, selective handles for further modification, ALD modifiers, and etch modifiers are reported.

**TF-ThP17 Effects of the Electric Field Application for the Photocatalytic Property of $TiO_2$/Nithin Films**, ***Taishi Segawa***, *I. Takano*, Kogakuin University, Japan

In recent years, titanium oxide has attracted attention for its various properties and has been studied in a wide application field such as solar cells or medical instruments. Particularly the photocatalytic effect of $TiO_2$ produces antifouling, antibacterial action or decomposing environmental pollutants such as nitrogen oxide because the photocatalytic reaction of $TiO_2$ generates the active species of superoxide anion or hydroxyl radical by using the energy of ultraviolet rays. One of the reasons why $TiO_2$ is the superior material as a photocatalyst is that the photo-excited state is very stable and does not cause autolysis. Therefore $TiO_2$ irradiated with ultraviolet rays can make the electrolysis of water stably proceed. On the other hand, the weak point of $TiO_2$ is that the absorption wavelength is limited to the ultraviolet region under 380 nm. Therefore, many researchers have studied to improve the efficiency of the light reaction of $TiO_2$. The distinctive point of our study is the energy supply of electricity during the light irradiation.

In this study, the glass substrates of 15×9 mm cleaned by an ultrasonic cleaner with acetone for 5 minutes were used. The $TiO_2$/Ni films were prepared by the multi-process coating apparatus with magnetron sputtering sources. The $TiO_2$ thin film preparation was carried out by sputtering a Ti target introducing an Ar and an $O_2$ gas. An Ar gas and an $O_2$ gas flow rate were set to 1.5 sccm and 20 sccm, respectively. The glass substrates were heated to 200 degrees by an infrared heater. The film thicknesses of $TiO_2$ and Ni were changed with 0 - 100 nm to investigate the suitable condition.

The crystal structure of each thin film was analyzed by X-ray diffraction. Optical properties were measured using a UV-Visible spectrophotometer. The photocatalytic properties were measured by the methylene-blue immersion test under irradiation of the artificial sunlight (visible light) and the sterilizing lamp. The change of the methylene-blue transmittance was measured with a spectrophotometer at leaguer intervals.

In the case of the artificial sunlight irradiation, the methylene-blue transmittance of the $TiO_2$/Ni (100/50 nm) film without the electric field application was 7 %, while that with the electric field application showed 45 %. Also in the case of irradiation with sterilizing lamp, the transmittance of the sample with the electric field application was 1.6 times as compared with that without the electric field application. The photocatalytic effect was improved by the electric field application during the light irradiation. The mechanism of effects by the electric field application to the sample will be examined in future.

**TF-ThP18 Investigations of Temperature and Humidity Sensors Constructed by Oxide Thin Films**, ***Takahisa Kawaguchi***, *I. Takano*, Kogakuin University, Japan

Currently commercial temperature and humidity sensors have a low sensitivity for both sides of a high and a low humidity. On the other hand, because the main parts of these sensors are manufactured using polymer materials, there is the problem of a short life in environments such as a high temperature or a high humidity. Therefore, the next-generation type sensors are required in a longer life and a higher sensitivity.

As a material satisfying some of the above-mentioned functions, $TiO_2$ was adopted in our study. $TiO_2$ is an n-type oxide semiconductor and has the stable photo-excited state as the material without autolysis. In addition, $TiO_2$ shows the hydrophilicity under ultraviolet light irradiation. The next-generation type sensor with a higher sensitivity is promised by constructing some oxide layers such as a $TiO_2$ layer or a $Cu_2O$ (p-type oxide semiconductor) layer.

In this study, basic investigations of $TiO_2$ and $Cu_2O$ thin films prepared by reactive magnetron sputtering were carried out about those physical properties and the multi-layer thin films were constructed to improve the sensitivity of temperature and humidity on sensor characteristics. The $TiO_2$/$Cu_2O$ thin film with each layer of 100 nm in a thickness and the $TiO_2$/$Cu_2O$/$TiO_2$/$Cu_2O$ thin film with each layer of 50 nm in a thickness were prepared by reactive magnetron sputtering.

The electric resistance of each sample was measured by changing the voltage from 0 V to 10 V. The resistance changes for temperature and humidity were measured about a range of the temperature from 25 degrees to 60 degrees and about a range of the humidity from 30 % to 60 %. Furthermore the water contact angle was measured by the q/2 method to investigate the relationship to humidity. In these experiments, the photoreaction on a semiconductor characteristic was examined by irradiating the White-LED light or UV-LED light to the sample surface.

The photo-excitation reaction of the $TiO_2/Cu_2O$ thin film was not confirmed by the light irradiation, because Cu atoms diffused to the $TiO_2$ layer. The temperature coefficient of resistance (TCR) of the $TiO_2/Cu_2O$ thin film and the $TiO_2/Cu_2O/TiO_2/Cu_2O$ thin film were $-16820\times10^{-6}$ [/K] and $-18400\times10^{-6}$ [/K], respectively. The resistance of the $TiO_2/Cu_2O/TiO_2/Cu_2O$ thin film was higher than that of the $TiO_2/Cu_2O$ thin film, because the number of an interface between a $TiO_2$ layer and a $Cu_2O$ layer influenced the bulk resistance of the thin film.

**TF-ThP19 Analysis of Surface Species and Film Structure of Thin Films from Atomic Layer Deposition using Surface-Enhanced Raman Spectroscopy**, ***Ryan Hackler***, *P. Stair*, *R.P. Van Duyne*, Northwestern University

*In-situ* surface-enhanced Raman spectroscopy (SERS) was used to identify dimeric methylalumina surface species during $Al_2O_3$ atomic layer deposition (ALD) on a silver surface. Vibrational modes associated with the bridging moieties of both trimethylaluminum (TMA) and dimethylaluminum chloride (DMACl) surface species were found during ALD. Density functional theory (DFT) calculations were also performed to locate and identify the expected vibrational modes. DMACl surface species were unable to be measured after multiple ALD cycles as a result of a loss in SERS enhancement and shift in LSPR. Currently, this work is being extended towards other ALD processes (such as $TiO_2$), as well as expanded to identify other characteristics of the thin films produced using adsorbate vibrational spectroscopy. This work highlights how *in-situ* optical spectroscopy by SERS and LSPR scattering are useful for probing the identity and structure of the surface species involved in ALD, as well as the structure of the resulting film.

**TF-ThP20 Carbon Thin Films Prepared by the Ion Assistance the Mass Spectrometric Analysis Type**, ***Kenji Iwasaki***, *I. Takano*, Kogakuin University, Japan

Recently, single-layer graphene sheets, diamond thin films, carbon nitride ($C_3N_4$) have attracted attention as a functional carbon thin film. Among them, DLC (Diamond-Like Carbon) is an amorphous carbon film showing characteristics which are close to that of diamond. Since those characteristics are high hardness, low friction coefficient, etc., DLC is used in a mechanical field such as sliding machine parts or engine parts.Practical application progresses rapidly in which tribology field, life expectancy has increased, maintainers

Contributing to Reducing Frequency In recent years, as a new characteristic of DLC gas barrier

Biocompatibility, etc. are recognized and it is expected to be applied to food containers, medical instruments, etc.

In our experiment, $Ar^+$, $N_2^+$, $He^+$ ion beam was used with evaporation to DLC films. This deposition method has some independent parameters from the film formation condition in comparison with other dry process methods. Therefore this method is anticipated in appearance of superior characteristics such as a high adhesion. In our previous research,

In our laboratory, we used $Ar^+$, $N_2^+$, $He^+$ as the ion species so far,

DLC film formation was carried out by an ion beam assist method in which toluene ($C_7H_8$) was introduced.

As a result of the investigation, by setting the ion species to $Ar^+$, the $sp^3$ ratio of the structure is maximized.

Although improvement of mechanical properties was expected, high-energy $Ar^+$ion irradiation turned out to be a factor of the increasing graphite structure. Therefore, further structural control is considered necessary to deposit DLC by low energy ions. In this study, we investigate various characteristics of DLC thin film by mass spectrometry type ion beam and compare it with DLC thin film with straight type ion beam.

**TF-ThP21 Supramolecular Heterostructures - Engineering Organic Layered Materials with Tuneable Fluorescent Properties**, *V.V. Korolkov*, The University of Nottingham, UK, *K. Watanabe*, *T. Taniguchi*, National Institute for Materials Science, Japan, ***Nicholas Besley***, *P.H. Beton*, The University of Nottingham, UK

For a long time the molecular self-assembly has been limited to engineering 2D molecular structures on surfaces. Here we demonstrate a successful approach that extends self-assembly into 3D by creating supramolecular heterostructures[1]. Essentially, these are layered organic materials that are stabilized by hydrogen bonds in plane and by van der Waals interactions between layers. Supramolecular heterostructures are formed by growing sequential layers of bi- and mono-component two-dimensional supramolecular arrays stabilized by hydrogen bonding. The heterostructures are formed on layered materials, hexagonal boron nitride (hBN) and graphite, by depositing layers of cyanuric acid/melamine (CA.M), 5,10,15,20-tetrakis(4-carboxylphenyl) porphyrin (TCPP), trimesic acid (TMA) and terephthalyc acid (TPhA).

We analyzed this heterostructures with ambient Atomic Force Microscopy that routinely achieve 0.1 nm resolution with conventional silicon probes. We have developed several approaches to characterize them. These include 'through-the-layer' imaging and scratching experiments to reveal the underlying layer structure.

AFM has confirmed that there is a clear epitaxial arrangement between these layers which intrinsically exhibit hexagonal (CA.M) and TMA, square (TCPP), linear (TPhA) symmetry. We demonstrate that heterostructure formation may be used to control the functional properties of supramolecular layers through a shift of the fluorescence peak position and a suppression of quenching for TCPP epitaxial layers.

The work will present outstanding examples of single molecule and submolecular resolution achieved in the ambient on standard atomic force microscopes. It is also possible to identify the registry between molecules in different layers and we include theoretical models which support our structural assignments and the observed shifts of fluorescent peaks.

[1] - *Korolkov et al.* **Nature Chemistry**, 2017, in press.

**TF-ThP22 Predicting Feature Size of AZ 9260 Positive Photoresist Processed by Two-photon Lithography**, ***Shelby Maddox***, *M. Zou*, University of Arkansas

Two-photon photolithography (TPP) is a promising fabrication method which allows very fine control over complex shapes in maskless lithography and is promising for creating 3D nanostructures. In this process, a high-fluence laser is focused into a photoresist in a discrete volume called a voxel. In the case of a negative photoresist, this volume is polymerized. In the case of a positive photoresist, the volume is monomerized. This size of this voxel depends on process parameters such as the focusing objective, the laser power, and the laser scanning speed across the photoresist surface. It is desirable to be able to precisely predict the feature width based on these process parameters. In this work, we present a mathematical model for predicting feature width created by a single-voxel using AZ 9260 positive photoresist with TPP. AZ 9260 is a high aspect ratio positive photoresist used in maskless lithography. The mathematical models are created which describe the resultant feature width as a function of the focusing objective, laser power, and the laser scanning speed. The features can be used as masks in a subsequent metal deposition to create conductive nanostructures for micro-electrode design, for use in biological research and multifunctional surfaces.

**TF-ThP24 ALD of Titanium Oxide using Cyclopetadienyl Titanium Alkylamide and Ozone**, ***Seongyoon Kim***, *J. Kim*, *T.R. Mayangsari*, *J.-M. Park*, Sejong University, Republic of Korea, *J.W. Park*, Hansol Chemical Co., Ltd., Republic of Korea, *W.-J. Lee*, Sejong University, Republic of Korea

Titanium-containing thin films are widely used in microelectronic device structures such as high-permittivity capacitors, barrier metals, and metal gate structures. ALD technology has replaced PVD and CVD to provide excellent step coverage, accurate film thickness control, and high film quality. Many organic titanium compounds such as alkylamido titanium compounds and cyclopentadienyl titanium alkoxides have been used as precursors. The preferred properties of such precursors include good thermal stability, high reactivity and sufficient volatility. In the present study, we investigated the ALD of titanium oxide by using cyclopentadienyl titanium alkylamide compound and ozone. Density functional theory calculation was used to predict the properties of precursors, and in-situ QCM and FTIR were used to investigate deposition rates and reaction mechanisms. The physical and electrical properties of the deposited films were also characterized.

**TF-ThP25 Characteristics of Ge-Sb-Te Film Prepared by Atomic Layer Deposition and Tellurization of Ge-Sb Film**, ***Yewon Kim***, *S. Kim*, *J. Gu*, *J.-M. Park*, Sejong University, Republic of Korea, *W. Koh*, UP Chemical Co., Ltd., Republic of Korea, *W.-J. Lee*, Sejong University, Republic of Korea

The phase change random access memory device is the next generation non-volatile memory device in the spotlight, especially storage class memory applications. Ge-Sb-Te (GST) compounds have been extensively studied due to their fast switching properties among the phase change materials. In particular, the pseudo-binary compositions between GeTe and $Sb_2Te_3$ attracted much attention. The GST thin films were prepared by physical vapor deposition, chemical vapor deposition and atomic layer deposition (ALD) techniques. Recent studies have focused on ALD of $Ge_2Sb_2Te_5$ film that combine ALD of GeTe with ALD of $Sb_2Te_3$, which is relatively complex. In this study, we prepared GST films by ALD and tellurization annealing of Ge-

Sb film as an alternative manufacturing method of GST film. This method simplifies the deposition sequence and allows easy control of the film composition. The composition profile, crystal structure and phase transition temperature were investigated by Auger electron spectroscopy, Raman spectroscopy and resistance change before and after tellurium annealing. Changes in resistance were discussed in terms of composition and crystal structure. Gapfilling of the deposited film was also observed before and after tellurization.

**TF-ThP26 Molecular Layer Deposition of Boron Carbide from Carboranes**, ***Michelle Paquette***, *L. Dorsett, S. Malik, T.D. Nguyen, D. Bailey, K. Rimpson,* University of Missouri-Kansas City, *J.D. Bielefeld, S.W. King,* Intel Corporation

Atomic layer deposition (ALD) research has exploded in this era of electronic miniaturization, smart materials, and nanomanufacturing. To live up to its potential, however, ALD must be adaptable to many types of materials growth. To extend the reach of this layer-by-layer deposition framework, researchers have begun to explore molecular based processes. Still relatively rare, existing molecular layer deposition (MLD) processes are typically based on the condensation of “linear” 2D or “brush-type” organic polymer chains. To move toward a 3D MLD growth model, precursors with multiple reaction sites would be desirable. To this end, icosahedral carborane ($C_2B_{10}H_{12}$) molecules provide an interesting target. Carboranes have been used in the plasma-enhanced chemical vapor deposition of boron carbide films for low-*k* interlayer dielectrics, neutron detection, and a variety of protective coatings. These are symmetric twelve-vertex molecules, wherein the terminal H atoms at each vertex are known to be labile in the presence of plasma, heat, or a number of chemical reagents. The carborane molecule is very stable and can be derivatized with a range of functional groups; dozens of these derivatives are available commercially, many of which have relatively high vapor pressures. As such, the carborane molecule is particularly intriguing as a novel MLD precursor for 3D growth, possessing unique symmetry, chemical reactivity, and volatility properties not commonly encountered in traditional organic molecules. In this contribution, we describe early work in our group toward developing a novel MLD process for the growth of boron carbide films using a number of different carborane precursors and substrates.

**TF-ThP27 Comparative Study of the Optical and Structural Properties of Single and Stacked SRO Thin Films Obtained by RF Sputtering**, ***Karim Monfil Leyva***, *A.S.L. Salazar Valdez,* Benemérita Universidad Autónoma de Puebla, Mexico, *A. Morales Sánchez, F. Morales Morales,* CIMAV-Monterrey, Mexico, *J.A. Luna López,* Benemérita Universidad Autónoma de Puebla, Mexico, *A.L. Muñoz Zurita,* Universidad Politécnica Metropolitana de Puebla, Mexico

Silicon rich oxide (SRO) has proved to be a cheap and interesting alternative to develop ultraviolet absorbers or silicon-based light emitters. New electronic and optoelectronic devices based on SRO material may require of single or stacked films with different silicon excess to improve optical and electrical properties. SRO films can be deposited by several deposition techniques but they can be obtained at Room Temperature by RF Sputtering deposition technique and its thickness can be well controlled. Silicon excess can be changed by fixing the RF-Power density on the $SiO_2$ target and changing the RF-Power on the Silicon target ($P_{Si}$).

In this work, we report a comparative study and analysis of the optical and structural properties of single and stacked SRO thin films obtained by RF Sputtering. Single SRO films were obtained by changing the $P_{Si}$ = 30, 40 and 50 W. Two different stacked SRO films, like a Bilayer (BL) structure, were obtained by changing the $P_{Si}$ = 50/30 W and 30/50 W. All samples were deposited on *n*-type silicon (Si) substrates with low resistivity (1~5 W•cm). A thermal annealing of 1100°C for 3 hours in $N_2$ ambient was applied to all SRO films. Step measurements were applied to calculate thickness of SRO samples. X-ray photoelectron spectroscopy (XPS) measurements were obtained from all samples to calculate and compare the Silicon excess. XPS results revealed the non-stoichiometric nature of our single SRO films and a change of Silicon excess in the BL structure. SEM images showed clear clusters on surface possible due to Si-nanocrystals (Si-nc) on bulk; also, surface roughness was calculated for all SRO films. Both BL structures showed Photoluminescence emission (PL) at Room Temperature (RT) before and after thermal annealing but the intensity was clearly increased after annealing. BL structures showed higher PL than single SRO films. All SRO samples showed two bands, a low blue band from 400 to 550 nm and a strong red band from 575 nm to 875 nm. Blue and red emission bands were related to Si-nc and defects in the SRO samples.

**TF-ThP28 Dependence of the Corrosion Behavior of Transition Metal Nitride Films on the Sputtering Power Mode**, ***Yuri Chipatecua***, CINVESTAV-Unidad Queretaro, Mexico, *O. Tengstrand,* Linköping University, Sweden, *J.J. Olaya-Florez,* Universidad Nacional de Colombia, *G. Greczynski,* Linköping University, Sweden, *I. Petrov, J.E. Greene,* University of Illinois at Urbana-Champaign, *A. Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico

Transition metal nitrides (TMN) are valuable coatings because they provide desirable properties of practical use. Their physical and chemical properties are also interesting from the fundamental perspective . Through the combination of sputtering power modes (HIPIMS and DCMS), it is possible to control, at least partially, harmful structures such as porosity, defects among grains, vacancies and dislocations.

We employed a hybrid high-power pulsed and dc magnetron co-sputtering with synchronized substrate bias to grow TMN films. Ti and Al were deposited in DCMS and Ta in HIPIMS mode. The bias was applied in synchronous with the Ta-ion portion of each HIPIMS pulse to minimize $Ar^+$ bombardment. TiN coatings were deposited in the modes of direct current (TiN_DC) and direct current pulsed (TiN_P) with a constant substrate bias. TiTaN, TiTaAlN, TiN_DC and TiN_P coatings were grown onto stainless steel AISI 304 with thickness ~ 300 nm. Corrosion studies were carried out in a NaCl solution at room temperature by electrochemical impedance spectroscopy and potentiodynamic polarization. By Tafel extrapolarization from the potentiodynamic curves, corrosion current density values ($I_{corr}$) were three orders of magnitude lower than substrate AISI 304. While TiN (DC and P) coatings showed degradation or products of corrosion accumulation, TiTaN and TiTaAlN coatings proved to be efficient as corrosion protection barrier. Their integrity was not affected (there was no evidence of microcracks, delamination or failure). This is probably associated to a more intense ion bombardment due to higher applied potential in the range of 4 to 6 kW. These coatings showed lower oxygen content than TiN_DC and TiN_P. The chemical composition of all coatings was evaluated by XPS sputter resulting in $Ti_{0.82}Ta_{0.35}N$ and $Ti_{0.30}Ta_{0.12}Al_{0.78}N$, respectively, both with a small amount of oxygen contamination (4%). In the case of titanium nitride, the composition was $Ti_{1.09}N\ O_{0.53}$ for DC mode and $TiN\ O_{0.24}$ for DC pulsed mode. The background associated to the Ti 2p spectra show an interesting behavior with composition. In this paper we will also discuss the relationship between corrosion and sputtering power mode.

**TF-ThP29 Laser Microstructuring of Gas Sensing Thin Films**, ***Premysl Fitl***, *J. Vlcek, D. Tomecek, E. Maresova, S. Havlova,* University of Chemistry and Technology Prague, Czech Republic, *M. Novotny, J. Lancok,* Institute of Physics ASCR, Czech Republic, *M. Vrnata,* University of Chemistry and Technology Prague, Czech Republic

Focused Laser beam is a widely used for deposition, localized annealing and patterning of various materials (eg. Metals, oxides, organic substances). Our work is focused to possibilities of usage of continuous wave (CW) lasers for local deposition and patterning of inorganic and organic semiconductors.

The source substrates were prepared as follows: Thin glass slides with sputtered metal layer (gold - thickness ~ 100 nm) were cleaned and dried. Side with sputtered metal was then covered with a thin layer of purified organic semiconductors – Zn, Pb and Fe Phthalocyanines, deposited by organic molecular evaporation in high vacuum chamber (10-5 Pa, dep. Rate ~ 0.1-3nm/min, substrate temp. 20 – 300 °C). The temperature of deposition source and substrate was selected for each substance so as to achieve optimal growth rate and to avoid thermal decomposition of materials. In the next step CW laser depositions were carried out from these substrates. The deposition apparatus include micro CNC machine (minimal step adjustable to 300 nm) equipped with the semiconductor laser (405 nm, 10 - 50 mW, spot 6 microns) in continual mode and focusing optics. The distance between source substrate and target (i.e. glass, silicon or alumina sensor substrates) was varied between 1-100 micrometers. Deposition process was held in an inert gas (Argon, Nitrogen) at atmospheric pressure. Morphology and microstructure were studied by optical, electron microscopy and AFM. Chemical composition of deposited structures was studied by FTIR and compared with that of source substances. It was proved that chemical structure of all chosen substances is not affected by this deposition technique. The best lateral resolution of prepared structures was obtained for source layer thickness of 100-150 nm. Employing our technique we are able to achieve precise and reproducible laser transfer of organic semiconductors to the target sensor substrate with lateral structural resolution of 14 microns.

We can make an assumption that our technique could be used also for other organic semiconductors used in gas sensors which can be deposited by organic molecular evaporation.

**TF-ThP32 Low Temperature Growth of $VO_2$ Films on Flexible Plastic Substrates using TiO2 Buffer Layer**, ***DaeHo Jung***, *H.S. So, J.S. Ahn, S.B. Hwang, H. Lee*, Kyung Hee University, Republic of Korea

Vanadium dioxide ($VO_2$) with high transmittance of visible-ultra violet radiation but the complete blockage of infrared solar radiation can be used for `solar control` windows. A thermochromic smart window is designed such that the $VO_2$ films regulate solar infrared radiation. Polyimide has thermal stability, good film-forming ability, low dielectric constant, high chemical resistance, low coefficient of thermal expansion and high mechanical strength. Due to these reasons polyimides are largely used as matrix for various purposes and the advantages of polyimide (PI) have been utilized as flexible substrate. $VO_2$ thin films with ~50 nm in thickness were grown on $TiO_2$-buffered PI films using RF magnetron sputtering deposition using a $VO_2$ target. The sputtering pressure was set at 6 mTorr with 10 sccm flow of Ar gas. $VO_2$ thin films on $TiO_2$-buffered PI films were grown at 175°C. Since the PI substrates (75 mm-thick) can keep physical properties only up to 260 °C, low temperature growth of $VO_2$ films (≤ 260°C) is necessary, After sputtering deposition, all samples were annealed with 1 sccm of $O_2$ flow for 1hr. The structural and morphological properties of all $VO_2$ films were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy. However, no peak for the monoclinic of phase of $VO_2$ appeared in Raman spectrum of growth of $VO_2/TiO_2$/PI at under 200°C. It was difficult to observe XRD diffraction peaks of $VO_2$ because $VO_2$ thin films did not crystallize under 200°C. The chemical compositions of $VO_2$ were probed by x-ray photoelectron spectroscopy. The measurement of depth-dependent O/V ratio also showed that the stoichiometry was independent of depth for $VO_2$ films.We measured the hysteresis curve of sheet resistance as a function of temperature. We measured the reflectivities of VO2 films below and above the metal-insulator transition temperature. The ratio of switching resistivity was $10^{-2}$. VO2 films grown on plastic films can be applicable as flexible thermochromic films for energy-saving windows.

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**TF-ThP33 Single Junction GaAs Thin Film Solar Cells on Flexible Metal Tapes for Low Cost Photovoltaics**, ***Devendra Khatiwada***, *P. Dutta, M. Rathi, S. Sun, Y. Yao, Y. Gao, Y. Li, S. Pouladi, J.-H. Ryou, V. Selvamanickam*, University of Houston

There is great interest in thin film solar cells for manufacturing cost-effective photovoltaics due to their advantages of light weight, versatile application, mechanical flexibility and scalable length. Thin film solar cells made of III-V semiconductor materials that have a high absorption coefficient over a wide range of the solar spectrum are strong candidates but have been largely unexplored so far. GaAs has high mobility, high band gap and high absorption coefficient and AlGaAs can be lattice matched with GaAs to form a heterojunction structure. While the highest efficiencies have been reported in III-V solar cells based on GaAs and Ge wafers, their application has been very limited due to high cost of these wafers.

Herein, we have developed high quality epitaxial semiconductor thin films on low-cost flexible metal tapes to overcome the wafer cost as well as benefit from the lower manufacturing cost of roll-to-roll processing. In our process, single-crystalline-like germanium films are grown on the flexible metal tape over which epitaxial (Al)GaAs semiconductor thin films are grown by metal organic chemical vapor deposition (MOCVD). The grown device architecture is further processed for contact deposition via photolithography.

The fabricated thin film III-V solar cells exhibit photon conversion efficiency of 7% with open circuit voltage ($V_{OC}$) of 565mV, short circuit current density ($J_{SC}$) of 17.9 mA/cm$^2$ and fill factor (FF) of 67% under A.M 1.5 (1 sun). Conversion efficiencies up to 11% have also been demonstrated with the thin film III-V solar cells. Further improvement in device efficiency is being pursued with new device architectures and optimization of the growth and fabrication processes.

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**TF-ThP34 Optical and Microstructural Characterization of Epitaxial $VO_2$ on $TiO_2$ (001) and Niobium Doped $TiO_2$**, ***Jason Creeden***, *I. Novikova, R.A. Lukaszew*, The College of William and Mary

The goal of this project is to optimize the efficiency of the optically induced insulator to metal transition (IMT) in the near-UV and UV regions, following the recent demonstration that $VO_2$ prepared on niobium doped $TiO_2$ ($TiO_2$:Nb) substrates can push the photoconductive response, ordinarily strong in the infrared, into the visible spectrum. Therefore, this project focused on the tailoring of the optical and microstructural parameters pertaining to the IMT in $VO_2$ thin films. This was done by controlling the microstructure of the films via deposition parameters and substrate doping and thus optimizing the $VO_2$ growth process for $TiO_2$ and $TiO_2$:Nb substrates. In doing so, we strained the monoclinic structure seen in the insulating phase toward the tetragonal structure seen in the metallic phase post-transition. The film composition was characterized via X-ray diffraction (XRD) and changes to the $VO_2$ optical transmissions, during the thermally induced IMT, were recorded using both a HeNe laser (1520 nm) and a 405 nm diode laser. With the HeNe laser, we could see strained bulk-like transitions of $VO_2$ occurring for samples grown on $TiO_2$ and small transitions for the samples grown $TiO_2$:Nb. The samples grown on $TiO_2$:Nb structurally exhibit a .25° shift in the XRD peak location in comparison to the un-doped samples. With the 405 nm laser, the samples grown on $TiO_2$:Nb exhibit sharp transitions that are comparatively large to those of the slight transitions seen in samples grown on $TiO_2$. Suggesting that the doping enhances the near-UV optical response of the film.

**TF-ThP35 Characterizing the Field of Atomic Layer Deposition: Authors, Topics, and Collaborations**, ***Elsa Alvaro***, Northwestern University, *A. Yanguas-Gil*, Argonne National Laboratory

Atomic layer deposition (ALD) has become one of the key techniques in thin film growth with applications in areas such as microelectronics, advanced sensors, energy storage, and more. Using a combination of bibliometric, social network, and text analysis, we describe the evolution of ALD as a field over time. In particular, we have examined the evolution in terms of publications, as well as changes in authors, journals, and collaborators.

The study of the collaboration network of ALD scientists over time shows how the ALD research community, originally consisting of small isolated clusters, becomes both larger and more interconnected. The formation of a single large connected component in the collaboration network coincides in time with the first AVS-sponsored symposium on the subject. As of 2015, the largest connected component spans 90% of the authors. In addition, the evolution of network centrality measures such as degree and betweenness centrality and author productivity allow us to identify the central figures in ALD according to each metric and their evolution over time, including the appearance of new "stars" in the last decade. Finally, we carried out a study of the title words of the papers in our dataset. Through the evolution of the technical terms in the titles we can map the evolution of the field. The results are consistent with a shift in focus on research topics towards energy applications and nanotechnology, and an increase in interdisciplinarity that correlates well with the evolution of the main scientific journals that publish ALD research.

**TF-ThP37 Nano-laminates Encapsulation Films Fabricated via Spatially Separated Atomic Layer Deposition for High Stable Flexible OLED Electronics**, *Y. Li*, ***Yuanyuan Liu***, *K. Cao*, Huazhong University of Science and Technology, China, *H. Hsu, J. Huang*, Wuhan China Star Optoelectronics Technology Co., Ltd (CSOT), China, *R. Chen*, Huazhong University of Science and Technology, PR China

The expansion demand for wearable and flexible electronics based on organic light emitting diode (OLED) displays have attracted great attention. Flexible OLED displays, however, widely utilize materials that are sensitive to oxygen and water which causes performance degradation or failure during usage. It is imperative to develop reliable and efficient thin film encapsulation methods to improve the stability and meet the requirements of miniaturization, flexibility and low cost. Atomic layer deposition (ALD) technique enables thin film fabrication with high quality, good uniformity and atomic level controllability in film thickness. It is quite promising as a practical method for future flexible electronics encapsulation.

This work focuses on the design and fabrication of encapsulation films for high stable flexible OLED electronics via spatially separated atomic layer deposition (S-ALD). S-ALD is proposed to separate different precursors' zones with inert gas in space ensure continuous deposition process. By optimizing the design of precursor injectors' structure and movement of sample stage, the uniformity and growth rate of deposited films are enhanced significantly. The oxides nano-laminates are fabricated with S-ALD method. The stacked sequence (ABAB, AABB) and thickness for every sub-layer are precisely controlled with ALD cycles. Recent research show that the water vapor transmission rate (WVTR) has been enhanced with nano-laminates compared with single layers with the same thickness. The WVTR is also influenced with the nano-laminates' structures as stacked sequence. Moreover, the organic sub-layers are introduced to form organic-inorganic multi-barriers to protect OLED devices. The composite encapsulate layers demonstrate both good bending mechanical properties as well as enhanced devices' stability towards hydrothermal aging.

**TF-ThP38 Conductive Collagen: A Novel Material for Green, Transient Implantable Electronics**, ***ArghyaKamal Bishal***, *C. Sukotjo, C.G. Takoudis*, University of Illinois at Chicago

In modern biomaterial based electronics, the choice of green and transient material is becoming attractive.[1, 2] This kind of materials require to have unique properties like biodegradability, bioresorbability, biocompatibility and environmentally safe.[1, 2, 3] The advantages behind using these materials are: low cost, energy efficient production due to their natural origin, no long term adverse effects, no need of retrieval as they can resorb and above all they can minimize hazardous waste for our environment.[2]

Collagen is an important biomaterial which is used in several biomedical applications. It has a triple helix structure made of polypeptide chains.[3, 4] Glycine, proline are the most abundant amino acids found in its structure. Collagen is a flexible biomaterial which is also biodegradable/bioresorbable[5], biocompatible[5] and piezoelectric[3] hence might be an ideal choice for this kind application in implantable electronics.

In this work, we present electrical properties of collagen membrane functionalized with a thin film deposited using Atomic Layer Deposition (ALD). For this study, a commercially available bioresorbable collagen membrane was used as ALD substrate. As a preliminary pilot study, thin film of titanium dioxide ($TiO_2$) was deposited on collagen membrane in a custom-made ALD reactor and different film thickness was achieved by varying the number of ALD cycles. The deposition was performed at room temperature using Tetrakis(dimethylamido)titanium (TDMAT) and ozone as metal precursor and oxidizer, respectively.[6] Electrical properties of the samples were measured using a 2-probe system. Preliminary results showed that the ALD coated collagen samples were more conductive compared to non-coated control and this conductivity increased with increase in number of ALD cycles.

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**TF-ThP39 Alkali Halide Assisted Atomic Layer Etching of Metal Oxides**, *J. Hennessy*, ***April Jewell***, *S. Nikzad*, Jet Propulsion Laboratory

The authors previously reported on the development and application of an atomic layer etching (ALE) procedure based on alternating exposures of trimethylaluminum (TMA) and anhydrous hydrogen fluoride (HF) implemented to controllably etch aluminum oxide. We have shown that conditioning the chamber with a thin film of lithium fluoride (LiF) enhances the ALE process, resulting in higher etch rates and better uniformity. We have hypothesized that the LiF participates in an intermediate reaction that promotes the loss of fluorine surface species and results in conformal layer-by-layer etching of aluminum oxide films. Etch properties were explored over a temperature range of 225–300 °C with the $Al_2O_3$ etch rate increasing from 0.8 to 1.2 Å per ALE cycle at a fixed HF exposure of 60 ms per cycle. We have since extended this work to include a variety of substrates (metal oxides) and etch enhancers (alkali halides). Preliminary results suggest that the TMA/HF chemistry is effective at etching hafnium oxide. Additionally, other alkali halide materials (e.g. KBr) behave as oxide etch enhancers, in some cases resulting in even higher etch rates than what was previously achieved with LiF.

**TF-ThP40 Tribocorrosion Behavior of Ti-6Al-4V Alloy Coated with TaN/Ta Layers in Two Simulated Body Fluids**, ***Jessica Estefania González Sevilla***, *M. Flores, R. Rosas, E. García*, Universidad de Guadalajara, Mexico

Ti-6Al-4V alloy is one of the most used materials in biomechanical industry due to the high corrosion resistance as well as its elastic modulus relatively close to that of bone tissue. This material also has excellent biocompatibility and its surface can be treated to promote osseointegration with the host tissue. However, suffer from a low wear resistance in dry and wet conditions. This work focuses on the synthesis of Tantalum Nitride and tantalum layers by magnetron sputtering on substrates of Ti-6Al-4V alloy. TaN and Ta coatings are biocompatible materials, both are chemically stable and TaN has high nanohardness, these properties make the coating of TaN/Ta resistant to the simultaneous attack of corrosion and wear. The structure and composition of coatings were studied by XRD and EDS techniques respectively. Raman spectroscopy and Scanning Electron Microscopy were used to analyze the wear track of the alloy and coated samples. The tribocorrosion tests were made in two different simulated body fluids. One made of deionized water plus salts with the same ions concentration than in human blood and other of Fetal Bovine Serum (FBS) and a compensatory ion solution to reach the ions concentration at blood. The load applied was between 0.5 and 2 N using a ball of Al2O3. Were measured the open circuit potential, friction coefficient and total lost material. The results showed a reduction of the wear, as a consequence of the TaN/Ta coating. The incorporation of proteins by means of FBS in the corrosive medium reduces the friction coefficient.

**TF-ThP41 The Leakage Current Reduction in Atomic Layer Deposition Of $Al_2o_3$-Inserted $Srtio_3$ Films for Metal-Insulator-Metal Capacitors**, ***Sang Hyeon Kim***, Seoul National University, Republic of Korea, *C.H. An*, Seoul National University, Korea, Republic of Korea, *D.S. Kwon, C.S. Hwang*, Seoul National University, Republic of Korea

The characteristics of atomic layer deposition (ALD) of $Al_2O_3$-inserted $SrTiO_3$ (STO) dielectric thin films were investigated in metal-insulator-metal capacitors for dynamic random access memory. STO thin films exhibit much higher dielectric constant compared with currently used $ZrO_2$-based films, but the leakage current density is generally higher due to their low band-gap energy. To decrease the leakage current density, ALD-$Al_2O_3$ cycles were included in the STO ALD at different positions of the stack. 1 to 5 cycles of $Al_2O_3$ were inserted in the top, bottom, or middle of the STO film. As a result, the leakage current of the STO thin film with a thickness of 8nm decreased from $10^{-6}$ A/cm$^2$ to $10^{-8}$ A/cm$^2$ at 0.8V. This improved the minimum attainable equivalent oxide thickness (EOT) of the (top) $RuO_2$/STO/Ru (bottom) capacitor from 1.0nm to 0.68nm, with an acceptable leakage current density (~8 X $10^{-8}$A/cm$^2$). The degree of leakage current decrease was dependent on the locations of $Al_2O_3$ insertion into the STO thin film during the ALD. The leakage current reduction was more effective when $Al_2O_3$ was deposited at the top portion of the STO film than when it was deposited at the bottom portion. Only one cycle of $Al_2O_3$ at the bottom location significantly decreased the crystallinity of the STO layer grown on top, and thus, the higher post-annealing temperature was required to achieve high crystalline quality, which simultaneously increased the leakage by possibly involving nano- and micro-cracks. The $Al_2O_3$ at the top location did not induce such adverse effect while leakage current suppression effect was achieved.

## Tribology Focus Topic
## Room: Central Hall - Session TR-ThP

## Tribology Poster Session

**TR-ThP1 Tribocorrosion Behaviour of Ti6Al4V Alloy Trated By Laser Shock Processing**, ***Roman Angel Rosas Meza***, *G. Gómez Rosas, M. Flores Martínez*, Universidad de Guadalajara, Mexico, *C. Rubio González*, Centro de Ingeniería y Desarrollo Industrial, Mexico, *J.E. González Sevilla*, Universidad de Guadalajara, Mexico

The Ti6Al4V alloy is used in biomedical industry, currently employed in prosthesis fixing screws, there are concerns regarding its metal ion release and material loss caused by tribocorrosion in a living being. The surface functionalization by laser could improve the osseous integration of TiAl4V and reduce the damage by fretting corrosion in these screws. In this work, the laser shock processing (LSP) with two different swept densities (2500 and 5000 pulses/cm$^2$) have been employed to know the behavior of the tribocorrosion resistance of Ti6Al4V with and without treatment. The laser used was a Nd:YAG with pulsed laser frequency of 10 Hz and wavelength of 1064 nm. The LSP configuration was the water jet mode without protective coating. The tribocorrosion tests were made with the sample immersed in a simulated body fluid containing synthetic body fluid (SBF) and bovine serum (BS) as corrosive medium, in a tribometer with reciprocating movement, using loads from 0.5 N to 1.5 N. In the tribocorrosion test was measured the evolution of open circuit potential and friction coefficient. The lost volume of the wear track was calculated using a stylus profilometer. Hole drilling test was used to measure the residual stress. The samples were characterized by means of Raman spectroscopy, scanning electron microscopy and x ray diffraction. The tribocorrosion behavior was analyzed as a function of the laser swept densities and the applied loads.

## 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.

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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.

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*** 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)

## Applied Surface Science Division
## Room: 13 - Session AS+MS-FrM

## Unlocking the Sample History: Forensics and Failure Analysis
**Moderators:** Karen Gaskell, University of Maryland, College Park, Matthew Linford, Brigham Young University

8:20am **AS+MS-FrM1 *In Situ* Diagnostics of the Coupled Mechanical and Electrochemical Degradation of High Capacity Electrode Materials in Lithium Ion Batteries**, ***Xingcheng Xiao***, General Motors R&D Center **INVITED**

Higher capacity in electrode materials (such as Silicon) is always accompanied by higher volume expansion. Most of the efforts to date in Si based electrodes have been focused on architectural design to avoid Si cracking. To achieve high current efficiency and long cycle life, the solid-electrolyte interface (SEI) must be mechanically and chemically stable despite the large volume-change. In this presentation, I will show you a comprehensive set of *in-situ* diagnostic techniques we developed to

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* **National Student Award Finalist**

understand the coupled mechanical/chemical degradation of SEI layers during cycling. Based on the learning from the in-situ diagnostics, I will discuss some coating design strategies to achieve high cycle efficiency and extend the cycle life of high energy density batteries for electrical vehicle applications.

### 9:00am **AS+MS-FrM3 A Novel Approach to Characterizing the Silicon Anode Electrolyte Interface in Lithium Ion Batteries**

***Caleb Stetson***, Colorado School of Mines, National Renewable Energy Laboratory, *C.S. Jiang, S. Harvey, K. Wood, G. Teeter, C. Ban, M. Al-Jassim,* National Renewable Energy Laboratory, *S. Pylypenko*, Colorado School of Mines

As the Lithium-ion battery (LIB) technology sector continues to develop, advances increasingly rely on innovative battery materials, particularly anode materials. Silicon has arisen as a frontier in anode material research mainly due to its high theoretical lithium capacity and the extensive knowledge regarding its processing and fabrication.

One of the principal challenges associated with the development of LIBs is the lack of understanding of the solid electrolyte interphase (SEI) layer that forms between the organic electrolyte and anode during the initial cycling of the battery. Formed from electrolyte decomposition products, this layer must be electronically insulating while still being permeable to lithium ions to allow for charge transport. This balance between differing properties is often difficult to maintain: if the SEI grows too thick, it loses its permeability to lithium; if it becomes too thin, the electronic resistance cannot be maintained and current will flow between the two electrodes. Measuring spatial variation in resistivity within this layer and correlating these data with chemical composition is of upmost importance to understanding SEI performance.

The SEI forms on the anode surface with thickness in the nanometer regime, which poses a challenge for finding the buried interface of the SEI with the Si anode. In order to locate and measure electronic properties at this interface, our group has utilized a scanning spreading resistance microscopy (SSRM) probe and scanner head to measure resistivity with nanometer-scale resolution. This system is installed in an argon glove box to minimize sample exposure to oxygen and humidity. The SSRM probe features a doped diamond-coated silicon probe that is both electronically conductive and wear resistant. The application of a sample-probe bias voltage while varying the force exerted on the probe in AFM contact mode allows for measurement of resistivity laterally and vertically.

Measurements of resistance vs. depth for SEIs demonstrate strong trends of resistance decrease as the probe penetrates deeper levels of the SEI. Several techniques are utilized to investigate the chemical composition at different depths of the SEI, including Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS). Combining resistance and chemical speciation data originating from specific depths provides an interesting basis for the study of SEIs and the evolution of Si anodes under different cycling conditions with distinct electrolyte solutions.

### 9:20am **AS+MS-FrM4 In situ Liquid SIMS Investigation of Ion Solvation in Electrolytes for Lithium Ion Batteries**

***Zihua Zhu***, *Y. Zhang, Z. Xu, M. Su, C. Wang, X.F. Yu, J.G. Wang*, Pacific Northwest National Laboratory

Ion-solvent interactions are of great fundamental and practical importance. However, many mysteries have long been existing in this field. For example, for the electrolytes used for Li ion batteries, preferential solvation and coordination number of a $Li^+$ ion are two interesting questions in hot debates so far. A major reason for above situation is lacking of reliable analysis techniques that can provide direct molecular information to elucidate ion-solvent interactions. In this work, in situ liquid SIMS was used to examine salt ion-solvent molecule interactions in several representative electrolytes used for Li ion batteries. Our data of the $LiPF_6$ in EC: DMC electrolyte show very strong molecular evidence that EC is preferentially solvated with $Li^+$, supporting previous ESI-MS and NMR results, but against recent Raman results. In addition, our data suggest that although the coordination number of a $Li^+$ ion can be as high as six in bulk electrolytes, three of them may be more stable than the remaining ones. In addition, it was observed that $Li^+$ and $FSI^-$ ions tend to well-separated in 1.0 M LiFSI in DME electrolyte, consistent with our MD simulation results. As a comparison, many ion clusters were observed in the same concentration of $LiPF_6$ in EC: DMC electrolyte. The above findings suggest that in situ liquid SIMS can provide key evidence for better understanding of the ion-solvent interactions in the electrolytes for Li ion batteries.

### 9:40am **AS+MS-FrM5 Determining Bulk and Interface Chemical Damage Regimes in XPS Depth Profiling using Cluster Ion Beams**

***Benjamin Schmidt***, *J. Newman, J.F. Moulder, J.E. Mann*, Physical Electronics

The development of gas cluster ion beams (GCIB) has provided fresh opportunities to study materials that exhibit chemical changes under monatomic argon ion bombardment during XPS surface cleaning or depth profiling. This is especially important as mixed inorganic/organic structures are increasingly used in applications such as OLED display devices and medical implants.

Several variables are available to fine tune cluster energy and size, which provides high levels of control to the user, but can present an overwhelming parameter space for practical use. For example, previous studies have shown that there is a relationship between the GCIB energy/atom and observed chemical changes. In the case of depth profiling bulk $HfO_2$, Barlow [1] observed that no change in Hf 4f peaks was detected for argon GCIB settings of 6 eV/atom, whereas a decrease to 2 eV/atom was required to minimize indium reduction in InAs. In a similar study on $HfO_2$, we observe similar results. By varying beam conditions, no Hf 4f reduction is observed at nominal 5.6 eV/atom, but is seen with an nominal 8 eV/atom beam. We discuss bulk and interface effects under these various conditions. For example, while no peak shape changes were observed in bulk $HfO_2$ at 5.6 eV/atom, reduced Hf oxide species are observed near the Si substrate, broadening the measured $HfO_2$/Si interface. We have investigated several other material systems, including polymers and Ti compounds, to provide guidance on general user settings.

[1] AJ Barlow, JF Portoles, PJ Cumpson. Observed damage during Argon gas cluster depth profiles of compound semiconductors. J App Phys 116, 054908 (2014)

### 10:00am **AS+MS-FrM6 In Situ Studies on Radiation Resistance of Nanoporous Metals**

***Jin Li****, Texas A&M University, *C. Fan*, Purdue University, *Y. Chen*, Los Alamos National Laboratory, *X. Zhang*, Purdue University

High energy particle radiation induces severe microstructural damage in metallic materials. Void swelling is a general consequence of radiation damage and can drastically degrade the mechanical integrity of irradiated materials. Nanoporous (NP) materials have great potentials to alleviate irradiation-induced damage due to their giant surface-to-volume ratio. Here we show, by using in situ Kr ion irradiation of nanoporous Au in a transmission electron microscope, nanopores shrink during radiation, and their shrinkage rate is pore size dependent. In addition, from temperature-dependent studies, we found that both defect density and nanopores evolve with radiation temperature. Higher temperature results in lower defect density and reduced shrinkage rate of nanopores. The sink strength of nanopores as a function of temperature is estimated. Moreover, NP Au exhibits significantly enhanced swelling resistance compared to coarse-grained Au. This study sheds light on the design of radiation-tolerant nanoporous metallic materials.

### 10:20am **AS+MS-FrM7 Surface Analysis in the World of Fine Art**

***Thomas Beebe, Jr.***, *Z. Voras, C. Goodwin, K. deGhetaldi, B. Baade, J. Mass*, University of Delaware **INVITED**

Connections between the science of surface analysis and the science of cultural heritage, such as it is, have been neither historically strong nor particularly productive, unfortunately for both fields. We are developing new collaborations aimed at changing this. Not all cultural heritage conservators adopt a scientific approach, and not all of those that do are willing to expand their scientific approaches to include surface-sensitive techniques such as XPS and TOF-SIMS, in many cases because their backgrounds have not led them to know about such methods. To be fair, we surface scientists don't have all the answers and often can't get them. Not all surface scientists are interested in pushing the boundaries of their sample types into such unconventional realms, and not all of those that are interested have the patience to develop the new sample-handling and sample-preparation techniques applicable to XPS and TOF-SIMS analysis, not to mention dealing with the ultra-small sample sizes of such precious works of art. This presentation will draw upon several recent examples from the speaker's research team to show how XPS and TOF-SIMS can be used to shed some light on mechanisms of chemical and physical degradation, proposed and applied methods of stopping such degradation, and proposed and applied methods of repairing such degradation. The examples will come from a range of paintings and other art objects spanning from the Italian Renaissance to the post-Modern era.

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*** ASSD Student Award Finalist**

11:00am **AS+MS-FrM9 Surface Characterization of Acrylic Artists' Paints After Wet Cleaning with Water-in-Oil Microemulsions.**, ***Michael Clark**, M. Keefe,* The Dow Chemical Company*, T. Learner,* The Getty Conservation Institute*, B. Ormsby,* Tate, UK*, A. Phenix,* The Getty Conservation Institute*, E. Willneff,* University of Leeds, UK

This paper reports on developments from collaboration between The Dow Chemical Company, Tate and the Getty Conservation Institute to improve cleaning systems for unvarnished modern painted surfaces. Increased use of new artistic paints since the 1950s has created a need for new cleaning approaches as traditional wet and dry cleaning systems have been found to be unsuitable in many cases.

This body of research has focused on the development of improved wet cleaning systems for artists' acrylic emulsion paints. The present study describes novel microemulsion systems based on water and mineral spirits, each formulated with different anionic or non-ionic surfactants. For this application, water-in-oil microemulsions were designed to capture the positive aspects of water-based cleaning systems (good pick-up and dispersion of soils; control over the conductivity and pH) while limiting, to a degree, the risks associated with exposure to aqueous cleaners. These notable cleaning solutions have been found to be very effective at removing surface soiling on acrylic paintings and other water sensitive works of art. A range of spectroscopic techniques have been employed to characterize the paint surface for changes induced treatment with different cleaning solutions. TOF-SIMS and XPS results show that trace amounts of surfactant residues from cleaning formulations remain on paint surfaces in some cases. Amounts vary depending on the surfactant type, inherent surfactant solubility, in addition to the clearance steps undertaken.

11:20am **AS+MS-FrM10 Surface and Depth Profiling of Soft Organic Thin Films. X-Ray Photoelectron Spectroscopy Study**, ***Tatyana Bendikov**,* Weizmann Institute of Science, Israel*, S.J. Hutton,* Kratos Analytical Ltd, United Kingdom of Great Britain and Northern Ireland*, R. Balgley, G. de Ruiter, M. Lahav, M.E. Van der Boom*, Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS) is uniquely suited for the direct characterization of nanomaterials and thin films in terms of layer thicknesses, elemental composition and, frequently, the depth-distribution profile of elements across the film. In general, XPS is limited to probe the top <15 nm of a sample, and for thicker structures a digging-like etching process is needed.

Recent advances in depth profiling of organic and biological materials are based on sputtering with large Argon ion clusters ($Ar_n^+$).[1] Unlike monoatomic ions ($Ar^+$), large cluster ions do not penetrate deeply into the material, therefore sputter material from the near-surface region only, leaving the subsurface layers undisturbed and undestroyed.

Here we present two examples of successful XPS depth profiling of composite metal-organic architectures self assembled on the pyridine terminated silicon/ ITO substrates. The samples consist of four main components: metal complexes ($[M(mbpy\text{-}py)_3][PF_6]_2$, M = Ru (**1**) or Os (**2**); $Pd(PhCN)_2Cl_2$ (**3**) and (1,4-bis[2-(4-pyridyl)ethenyl]benzene, **BPEB**, (**4**) spacer molecules.

The first system was prepared by sequential immersion of the substrate in solution **1** (alternating with solution **3**) (4 layers) followed by **2** (alternating with **3**) (4 layers). Each layer is ~ 6 nm thick, thus the consequent total thickness of the organic film reaches 40-50 nm.[2]

In the second example molecular assemblies consist of different layers of metal complexes **1** and **2**, separated by repetitive spacers **4** alternated with **3**. Total thickness of the analyzed **[Ru-BPEB$_{12}$-Os]** assembly is ~20 nm.[3]

1. P. J. Cumpson et. al., *Surf. Interface Anal.*, **2013**,45, 1859-1868.

2. G. de Ruiter et. al., *J. Am. Chem. Soc.*, **2013**, 135, 16533-16544.

3. R. Balgley et. al., *J. Am. Chem. Soc.*, **2016**,138, 16398-16406.

## Plasma Science and Technology Division
## Room: 23 - Session PS+NS+SS+TF-FrM

## Atomic Layer Etching II
**Moderator:** Edward Barnat, Sandia National Laboratories

8:20am **PS+NS+SS+TF-FrM1 Quasi-Atomic Layer Etching of Silicon Nitride with Independent Control of Directionality and Selectivity**, ***Sonam Sherpa**, P.L.G. Ventzek, A. Ranjan,* Tokyo Electron Limited

Atomic layer etching (ALE) has emerged as a viable approach to address the challenges associated with continuous or quasi-continuous plasma processes. To this end, we previously reported the quasi-atomic layer etching of silicon nitride via sequential exposure to hydrogen and fluorinated plasma. The underlying premise was the surface modification via implantation of hydrogen ions into silicon nitride resulting in an anisotropic etch.

In this talk, we will demonstrate that similar enhancement in reactivity of silicon nitride can also be attained via diffusion of hydrogen atoms into silicon nitride with the resultant etch being isotropic. These results confirm the realization of self-limiting etch of silicon nitride with tunable directionality. This tuning capability is critical for sub-7nm technology node. Illustrations of anisotropic (spacer RIE for self-aligned multiple patterning) and isotropic (spacer RIE for nanowire FET) etch by using this process will also be discussed. Selectivity to oxide is > 100 and damage to underlying silicon can be minimized by optimizing the flux of atomic fluorine during the exposure to fluorinated plasma. Thus, hydrogen plasma controls the directionality while fluorinated plasma step determines the selectivity to oxide and underlying silicon.

8:40am **PS+NS+SS+TF-FrM2 $WO_3$ and W Thermal Atomic Layer Etching Using "Conversion-Fluorination" and "Oxidation-Conversion-Fluorination" Etching Mechanisms**, ***Nicholas Johnson**, S.M. George,* University of Colorado at Boulder

Atomic layer etching (ALE) of metals is important for the controlled removal of many valuable semiconductor materials such as conductors (e.g. W, Cu), metal gates (e.g. Ta, Ti) and metals in magnetic multilayers (e.g. Co, Fe). However, few reports exist for metal ALE using either plasma or thermal processes. Conventional thermal ALE that has defined recent work on metal oxide [1] and metal nitride [2] materials does not work for metals. New reaction pathways are required to etch metals. This study targets W ALE and examines both $WO_3$ ALE and W ALE as W oxidation to $WO_3$ is needed to define self-limiting reactions for W ALE.

$WO_3$ ALE was demonstrated using an AB exposure sequence with boron trichloride ($BCl_3$) and hydrogen fluoride (HF). $BCl_3$ and HF etch $WO_3$ by a "conversion-fluorination" mechanism. The $BCl_3$ converts the $WO_3$ surface to a $B_2O_3$ layer while forming volatile $WO_xCl_y$. HF then spontaneously etches the $B_2O_3$ layer producing volatile $BF_3$ and $H_2O$ products. $WO_3$ films were formed by oxidizing W ALD films with an oxygen plasma at 280ºC. *In situ* spectroscopic ellipsometry (SE) studies determined that the $BCl_3$ and HF reactions were self-limiting versus exposure. $WO_3$ ALE etch rates increased with temperature from 0.55 Å/cycle at 128°C to 4.19 Å/cycle at 207°C. W served as an etch stop because $BCl_3$ and HF could not etch the underlying W film.

W ALE was performed using a three-step "oxidation-conversion-fluorination" mechanism. This is an ABC exposure sequence that where the W surface is first oxidized to a $WO_3$ layer and then the $WO_3$ layer is etched with $BCl_3$ and HF. SE could simultaneously monitor the W and $WO_3$ thicknesses and conversion of W to $WO_{3.}$ Oxidation of the W surface was performed using $O_3$. SE measurements showed that the W film thickness decreased linearly with number of ABC reaction cycles. W ALE was shown to be self-limiting with respect to each part of the ABC process. The etch rates for W ALE were 2.4 Å/cycle at 207°C. An oxide thickness of ~20Å remained during W ALE, but could be removed with $BCl_3$/HF without affecting the W layer.

[1] Younghee Lee, et al., "Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of $Al_2O_3$ Using Sequential, Self-Limiting Thermal Reactions", *Chem. Mater.* **28**, 2994-3003 (2016).

[2] Nicholas R. Johnson, et al., "Thermal Atomic Layer Etching of Crystalline Aluminum Nitride Using Sequential, Self-Limiting HF and $Sn(acac)_2$ Reactions and Enhancement by $H_2$ and Ar Plasmas", *J. Vac. Sci. Technol. A* **34**, 050603 (2016).

9:00am **PS+NS+SS+TF-FrM3 Solving the Grand Challenges of Plasma Etch with Concurrent Engineering**, ***Mingmei Wang**,* TEL Technology Center, America, LLC*, P.L.G. Ventzek, A. Ranjan*, Tokyo Electron Limited **INVITED**

A consequence of multiple patterning approaches enabling Moore's Law scaling to continue through 10nm to 7nm and beyond is that plasma dry etch process faces unprecedented challenges. "Scaling" of plasma etch to seemingly impossible capabilities is the key to meeting Moore's Law scaling. For example, etch process must achieve extremely high (almost infinite) selectivity in applications where self aligned patterning schemes are involved. Etch process is also required to achieve less than half nanometer (atomic scale) CD variations across 300mm wafers including the important "extreme edge" area as small as 2mm exclusion. These are but two examples of etch grand challenges. While the process requirements push the hardware design to the limits, understanding of process mechanisms becomes the most critical bottleneck to explore process regimes that are able to satisfy the most challenging patterning requirements. In fact, without process understanding at the atomic scale, it is difficult to imagine a means to innovate hardware designs.

In this talk, we will discuss concurrent engineering approaches including both modeling and experiment to understand and develop etching processes that meet grand challenge requirements. The core of the approach is an integrated chamber scale HPEM (Hybrid Plasma Equipment Model)-feature scale MCFPM (Monte Carlo Feature Profile Model) model [1]. The concurrent engineering approach comprises stages of development and prediction capability tests using both blanket wafer and patterned stack data and finally process parameter optimization. By using this approach, we are able to provide insights on how to resolve grand challenges in plasma etch with a minimum of engineering resources. The presentation will survey both experimental and computational results representing a few case studies in SAC quasi-ALE [2], Si ALE, organic etch CD uniformity, and LER/LWR improvement in EUV resist patterned sample etch. Furthermore, insights into the relationship between chamber function and critical surface interactions will be discussed.

[1] M.Wang and M.Kushner, J. Appl. Phys 107, 2010.

[2] M.Wang, P. Ventzek, A. Ranjan, J. Vac. Sci. Technol. A 35, 2017.

9:40am **PS+NS+SS+TF-FrM5 Effect of Non-Uniform Polymer Deposition on the Atomic Layer Etching of 3D Features in $SiO_2$**, ***Chad Huard***, University of Michigan, *Y. Zhang, S. Sriraman, A. Paterson,* Lam Research Corporation, *M.J. Kushner,* University of Michigan

Atomic layer etching (ALE) typically separates the etch process into (at least**)** two self-limited steps, repeated cyclically – a passivation and an etch step. To obtain all of the benefits of ALE, each of the steps should be fully self-limited, and produce no continuous etching during either step. Only by the synergy between the two steps being repeated cyclically is atomic etching achieved. ALE etching mechanisms have been demonstrated for several materials (e.g., Si, Ge) that do not involve thick passivation layers. ALE-like etching has also been demonstrated for $SiO_2$ and $Si_3N_4$, however with the etching mechanisms for these materials relying on the non-self-limited deposition of a polymer layer, it is more difficult to obtain the full benefits of ALE in these systems.

To investigate the benefits and limitations of using an ALE-like pulsing scheme for etching $SiO_2$, a representation of the through-polymer etching mechanism of $SiO_2$ in $Ar/C_4F_8/O_2$ plasmas was developed and implemented into the 3-dimensional Monte Carlo Feature Profile Model (MCFPM). The model includes diffusion of radical atomic species (F and O) through the polymer capping layer and ion-energy activated reactions at the $SiO_2$/polymer interface stimulated by ions implanting through the polymer capping layer. These processes allow for the simulation of $SiO_2$ (and Si) etching through a finite thickness of polymer. The model reproduces systematic trends for selectivity and etch rates as a function of polymer thickness observed for continuous etching.

Results from the model suggest that the non-self-limited nature of the polymer deposition step can limit the benefits of applying ALE techniques to $SiO_2$, particularly in 3D features. The balance of polymer deposition by radical $CF_x$ species and erosion by F radicals is subject to neutral transport issues and so are more sensitive to geometry and aspect ratio than for fully self-limited passivation, as occurs in ALE of Si using, for example, $Cl_2$ containing gases. The reactive sticking coefficients of $CF_x$ radicals on the polymer surface depends, in part, on ion generated dangling bonds which can result in a non-uniform polymer thickness in 3D features. The etch depth per cycle (EPC) was found to depend on polymer thickness, introducing non-uniformity and aspect ratio dependent etch rates in 3D features during ALE. Methods for mitigating the dependence of EPC on polymer thickness using carefully controlled ion energies and the introduction of $O_2$ will be discussed.

Work was supported by Lam Research Corp., DOE Office of Fusion Energy Science and the National Science Foundation.

10:00am **PS+NS+SS+TF-FrM6 Etching with Low Te Plasmas**, ***Scott Walton****, D.R. Boris, S.C. Hernández,* Naval Research Laboratory, *S.G. Rosenberg,* ASEE Postdoctoral Fellow, NRL, *H. Miyazoe, A.V. Jagtiani, S.U. Engelmann, E.A. Joseph*, IBM T.J. Watson Research Center

Processing with atomic layer precision requires the ability to not only add, remove or modify one monolayer of material but to also leave adjacent layers unchanged. This requires fine control over the flux of species and energy deposition at the surface. The appropriate threshold and process windows are certainly material specific but it is reasonable to assume many applications require low energy ions. Electron beam-generated plasmas are generally characterized by high charged particle densities ($10^{10}$- $10^{11}$ $cm^{-3}$), low electron temperatures (0.3 - 1.0 eV), and in reactive gas backgrounds, a relatively low radical production rate compared to discharges. The flux at the surface will thus be characterized by a comparatively large amount of ions whose energies are < 5 eV, a value commensurate with the bond strength of most materials. Ion energies can be raised with substrate biasing, which makes these sources well-suited to meet the needs of energy requirements for precise, selective etching. In this work, we discuss SiN etching using pulsed, electron beam generated plasmas produced in $SF_6$ backgrounds. We pay particular attention to the etch rates, selectivity (vs. carbon films, Si and $SiO_2$), and patterning as function of operating parameters such as relative gas concentration, operating pressure, and substrate bias. These results are compared with plasma diagnostics to gain a better understanding of the process requirements and windows for threshold etching of SiN. This work is partially supported by the Naval Research Laboratory base program.

10:20am **PS+NS+SS+TF-FrM7 Thermal Atomic Layer Etching of Titanium Nitride Using Sequential, Self-Limiting Oxidation and Fluorination Reactions**, ***Younghee Lee****, S.M. George*, University of Colorado at Boulder

Titanium nitride (TiN) is an important conducting material as a copper diffusion barrier and a gate electrode in semiconductor devices. Previous thermal atomic layer etching (ALE) studies have shown that TiN was not etched using fluorination and ligand-exchange reactions [1]. These results suggest that the ligand-exchange reactions do not produce stable and volatile reaction products.

In this work, a new etching mechanism based on sequential, self-limiting oxidation and fluorination reactions was developed for thermal TiN ALE. The oxidation reactant was either $O_3$ or $H_2O_2$. The fluorination reactant was hydrogen fluoride (HF) derived from HF-pyridine. In the proposed reaction mechanism, the $O_3$ reaction oxidizes the surface of the TiN substrate to a $TiO_2$ layer and produces gaseous products such as NO. HF exposure to the $TiO_2$ layer then yields $TiF_4$ and $H_2O$ as volatile reaction products. The overall reaction can be written as: $TiN + 3O_3 + 4HF \rightarrow TiF_4 + 3O_2 + NO + 2H_2O$.

Quartz crystal microbalance experiments showed that HF can spontaneously etch $TiO_2$ films. Spectroscopic ellipsometry and x-ray reflectivity analysis showed that TiN films were etched linearly versus the number of ALE cycles using $O_3$ and HF as the reactants. The etch rate for TiN ALE was determined at temperatures from 150 to 350°C. The etch rates increased with temperature from 0.06 Å/cycle at 150°C to 0.20 Å/cycle at 250°C and stayed nearly constant for temperatures ≥250°C

The thermal ALE of many other metal nitrides should be possible using this new etching mechanism based on oxidation and fluorination reactions. This thermal ALE mechanism should also be applicable to metal carbides, metal sulfides, metal selenides, and elemental metals that have volatile metal fluorides.

[1] Y. Lee, C. Huffman and S.M. George, “Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions”, *Chem. Mater.* **28**, 7657 (2016).

10:40am **PS+NS+SS+TF-FrM8 Atomistic Simulations of $H_2$ Plasma Modification of SiN Thin-Films for Advanced Etch Processes**, ***Vahagn Martirosyan****, E. Despiau-Pujo, O. Joubert*, LTM, Univ. Grenoble Alpes, CEA-LETI, France

Due to high ion bombardment energies and significant fragmentation rates, conventional continuous wave (CW) plasma processes are not able to selectively etch ultra-thin films without damaging the active layers of advanced nanoelectronic devices. In particular, silicon nitride or low-k spacers etching must be performed with nanoscale-precision without creating defects to the underlayer substrate, to preserve device performances and be compatible with epitaxial steps. To solve this problem, one possible alternative is to use a recently developed etch technology, which consists of two steps [1]. In the first step, the material to be etched is exposed to a hydrogen (H2) or helium (He) ICP or CCP plasma; in the second step, the modified material is chemically etched by wet cleaning or exposure to gaseous reactants only.

Due to the complexity of plasma-material interactions, the successful development of such a new etch approach requires a more detailed understanding of the fundamental mechanisms involved in the process. Therefore, we develop Molecular Dynamics (MD) simulations to study the Si-N-He and Si-N-H systems and provide an overview of the reaction processes at the atomic scale. The objective is to understand the role of ion energy in the self-limited ion implantation, and to determine the relationship between the flux/energy of plasma species bombarding the surface and its chemical/structural modifications.

In this work, we investigate the interaction between hydrogen plasma species (Hx+ ions and H radicals) and silicon nitride via MD simulations. We first study the impact of ion energy (5-100eV), ion dose and ion type on a SiN substrate only exposed to ion bombardment. Then, the influence of a mixed exposure to both Hx+ ions and atomic H is investigated to observe how the hydrogen plasma composition will affect the SiN substrate modification. For pure ion bombardment conditions, simulations show an initial Hx+ ion implantation followed by the formation of a stable modified layer at steady state. Few or no SiN etching is observed for ion energies >25eV, which shows that hydrogen ions only induce a volume transformation and can modify the SiN substrate on a precise depth without etching it. By contrast, simulations of mixed ion/radical bombardment show that a high concentration of atomic hydrogen can crucially change the evolution of the substrate, since H radicals are able to slowly etch SiN along with the modification caused by Hx+ ions. Mechanisms of aforementioned phenomena, as well as comparison with experiments, will be discussed during the presentation.

1. N. Posseme, O. Pollet, S. Barnola, Applied Physics Letters 105, 051605 (2014)

11:00am **PS+NS+SS+TF-FrM9 Defectless Nanostructure Patterning of Germanium Using Neutral Beam Etching for Ge FinFET Devices**, ***Shuichi Noda***, Tohoku University, Japan, *W. Mizubayashi*, *K. Endo*, AIST, Japan, *S. Samukawa*, Tohoku Univeversity, AIST, Japan

Germanium FinFET has been becoming a promising candidates for highly scaled CMOS FETs due to large carrier mobility. However, etching mechanisms of Ge and optimization of etching method have not investigated deeply. We have already succeeded to apply a neutral beam etching (NBE) method to Si FinFET fabrication processes and shown excellent device performances owing to low-damage properties of NBE [1]. Since Ge is much more unstable material to apply to FET devices than Si, there must be much more advantages to use NBE method.

The NBE system consists of an inductive coupled plasma (ICP) source and a carbon aperture plate (neutralization plate) on which enormous number of high aspect ratio aperture holes are opened. Positive and negative chlorine ions generated in a pulse time modulated ICP are accelerated toward the aperture plate and effectively converted to the neutral beam by applying rf field on the aperture plate. Etching substrates beneath the aperture plate are etched mainly by directional chlorine neutral beams without any risky matters such as charged particles (electrons and ions) and irradiation of vacuum ultra-violet (VUV) light. We consider that the VUV irradiation has notable effect on the etching characteristics and defect generation that influences device performances.

We compared etching characteristics of Ge between the NBE and a plasma etching using the same ICP source. It was found that the Ge etching rate of NBE was about one order of magnitude smaller than that of the plasma etching. We consider that such a large differences is caused by surface defects induced by the VUV irradiation. Under the VUV irradiation, surface defects, that is high density dangling bonds of Ge, are created and the defect sites react with chlorine radicals actively and the chlorinated layer are etched off by the ion bombardment in the case of the plasma etching. On the other side, the Ge surface exposed to the neutral beam seems to be chlorinated more slowly and probably the chlorinated layer is much thinner than the plasma-like conditions. And the etching reaction occurs by the chlorine neutral atom beam bombardment. This smaller etch rate around 20 nm/min seems a little bit inefficient however it can be said this small etch rate is much more useful characteristics for the nanometer scale low damage etching processes. AFM observation showed that the etched surfaces by NBE were much smoother than that by the plasma etching. Etched side wall (to be Ge channel surface) by NBE were also very smooth and vertical. High magnification TEM images showed substantially atomic revel smooth side wall.

[1] K. Endo *et al.*, IEDM Tech. Dig. (2005) pp. 840-843.

11:20am **PS+NS+SS+TF-FrM10 Thermally-Driven Atomic Layer Etching of Metallic Tungsten Films Using $O_2$ and $WF_6$**, ***Wenyi Xie***, *P.C. Lemaire*, *G.N. Parsons*, North Carolina State University

The semiconductor industry is facing the challenge of manufacturing transistor devices with sub-10 nm high aspect ratio features. Understanding and developing self-limiting etching processes that allow precise control over the thickness of materials removed is essential for enabling the manufacturing complex transistor structures. In this work, we investigated chemical vapor etching of tungsten films using oxygen ($O_2$) as the oxidant source and tungsten hexafluoride ($WF_6$) as the etchant.

We propose that etching of tungsten proceeds in two steps: 1) oxidation of the tungsten film to form $WO_x$ surface species and 2) formation and removal of volatile metal fluoride species upon reaction with $WF_6$. Using quartz crystal microbalance (QCM), we found that the oxidation step with $O_2$ is required for etching to occur during $WF_6$ exposure. In addition, etching of $O_2$ treated tungsten films showed saturation towards $WF_6$ exposure. This indicates that etching of tungsten using oxygen and $WF_6$ is a self-limiting process, making it promising as an atomic layer etching process. QCM results also showed that the rate of etching depends on the temperature. Minimal amount of etching was measured at temperatures less than 275 °C. Ex-situ characterization techniques were applied to analyze the etching of tungsten films deposited on $SiO_2$ substrates. Scanning electron microscopy (SEM) results revealed the change in morphology of tungsten films after different number of $O_2$-$WF_6$ ALE cycles. The tungsten film on $SiO_2$ started out as a coalesced film, which transformed into disjointed nuclei, and the nuclei appeared completely removed as the number ALE cycle increased. Lastly, X-ray photoelectron spectroscopy (XPS) analyses further confirmed etching of tungsten film and showed a minimal amount of fluorine remained on the surface after the $O_2$-$WF_6$ ALE process.

## Surface Science Division
## Room: 24 - Session SS+HC-FrM

## Recent Advances in the Chemistry and Physics of Interfaces

**Moderators:** Robert Bartynski, Rutgers, the State University of New Jersey, Wei Zhao, University of Washington

8:40am **SS+HC-FrM2 Enantiospecific Chemistry of Aspartic acid on Copper Surfaces**, ***Soham Dutta***, Carnegie Mellon University, *A. Gellman*, Carnegie Mellon University, W.E. Scott Institute for Energy Innovation

Chirality is a geometric property and refers to existence of handedness in any system. While chirality is ubiquitous in nature across all spatial scales, chirality at the molecular level is of special interest given the homochirality of biomolecules such as DNA and the amino acids that are the molecular basis of life. Increasingly, fundamental research is focused on studying chiral molecules adsorbed on surfaces given their applications in enantioselective chemical phenomena such as heterogeneous catalysis. While many examples of 2D chiral assembly of molecules have been studied over the years, fundamental questions about chiral aggregation on surfaces remain unanswered. One such question is whether enantiomers deposited on a surface aggregate into domains containing enantiomers of the same chirality (homochiral) or domains containing both enantiomers (heterochiral).

In this study, we have used a combination of Temperature Programmed Reaction Spectroscopy (TPRS) and isotopic labelling to study the decomposition kinetics and aggregation behavior of aspartic acid (Asp) enantiomers on Cu surfaces. The ionization state of adsorbed Asp monolayer was determined to be anionic using X-ray photoelectron spectroscopy. Next, using isotopic labelling, we have identified Asp decomposition mechanism in greater detail than possible for any comparable size adsorbate on a metal surface. It was found that Asp follows a multi-step decomposition process to form $CO_2$ and acetonitrile. Then, the first observed enantiospecific decomposition of Asp enantiomers is reported on naturally chiral $Cu(643)^{R\&S}$. Lastly, equilibrium adsorption experiments of Asp enantiomer mixtures on copper surfaces were performed and Asp enantiomers was found to aggregate on the surface. A cluster-adsorption model was developed to quantify the free energy change and equilibrium constants of enantiomer aggregation in 2D for the first time.

The combination of a surface explosion pathway with a naturally chiral catalytic surface leads to high enantiospecificity of Asp decomposition. This non-linear explosive decomposition pathway, coupled with the availability of multiple isotopomers is exploited to quantitatively probe aggregation behavior of aspartic acid with unprecedented detail.

9:00am **SS+HC-FrM3 Anchoring Carbon Nanotubes to Solid Supports via Direct Attachment Through the Cage**, ***Mackenzie Williams****, *F. Gao*, University of Delaware, *I. Ben Dhiab*, Université Pierre et Marie Curie, *A.V. Teplyakov*, University of Delaware

The unique physical, optical, and electronic properties of carbon nanotubes (CNTs) have resulted in their integration into devices for a myriad of applications. For this reason, a great number of studies have focused on the many existing methods of chemical attachment of these structures to various support materials. Carbon nanotubes are typically anchored onto these substrates through additional functional groups, such as carboxylic acids, that are present on the CNT edge or defect sites. This typically results in vertical orientation of the CNTs on the surface and the extra linkages of these functional groups may affect the electronic transfer processes through the structure. This may be desired in some cases; however in others, it is preferable to increase the surface contact between CNT and substrate or to preserve the original electronic structure of the CNTs. To this end, we have focused our efforts on direct attachment of CNTs to surfaces. The work described here finds that these extra functional groups on the CNTs are not the only way through which CNTs can bind covalently to a substrate. In fact, the presence of functional groups is not necessary at all for covalent attachment to the surface to occur. Carbon nanotubes containing no additional functional groups were attached to amine-modified gold and silicon substrates directly through the cage structure, similarly to direct attachment that has been found to occur through other caged structures such

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* **National Student Award Finalist**

as C$_{60}$ buckyballs. Microscopy techniques were used to confirm the presence of CNTs in intimate contact with the surface and X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry were used to investigate the chemistry involved. Through comparison to multiple controls, including carboxylic acid-modified CNTs, it was determined that covalent attachment can occur directly through the cage of the CNT. Density functional theory computational methods were used to predict core level binding energies and to confirm the feasibility of this process.

9:20am **SS+HC-FrM4 Studying Trends in Aromatic Adsorption on Fe{110} using Density Functional Theory Calculations**, ***Bianca Provost***, University of Cambridge, UK, *M.Y. Ho, T.L. Hughes,* Schlumberger Gould Research, UK, *J.M. Goodman, S.J. Jenkins*, University of Cambridge, UK

Aromatic adsorption on metal surfaces plays a key role in many fields including heterogeneous catalysis, electrochemical devices, photovoltaics, corrosion protection and chemical sensing. Benzene and to a lesser extent larger aromatic systems have been studied on a variety of metal surfaces both computationally and experimentally.[1-3] However, one metal surface which has received very little attention for aromatic adsorption is iron. Experimental UHV adsorption studies carried out on iron surfaces are complicated by the metal's reactivity and strong tendency to passivate, which result in significant difficulty obtaining a high purity metal surface. Still, iron is deserving of study as it is the major component of steel and catalyses important industrial reactions such as the Fischer-Tropsch and Haber processes. A computational study of the surface chemistry of aromatic molecules on iron will provide novel insight on these systems as well as a level of detail which would not be afforded using experimental techniques.

We have carried out a density functional theory (DFT) study of benzene, naphthalene and quinolinium adsorption on the most stable and therefore predominantly exposed surface facet of a bcc iron crystal, Fe{110}. All identified stable adsorption sites are presented and the most energetically favourable sites are compared across all three studied adsorbate-surface systems. To support the energetic and geometric results of our study, charge density differences, residual spin densities, density of states (DOS) and work function changes have also been calculated and analysed. Finally, we have studied the effect of van der Waals corrected DFT on binding site energetics and geometries. Such corrections have been shown to provide results in better agreement with experiment for aromatic adsorption on certain metal surfaces.[1]

[1] Carrasco, J., Liu, W., Michaelides, A., Tkatchenko, A. *J. Chem. Phys.* **2014**, 140, 084704

[2] Jenkins, S. J. *Proc. R. Soc. A* **2009**, 465(2110), 2949-2976

[3] Netzer, F. P. *Langmuir* **1991**, 7(11), 2544-2547

9:40am **SS+HC-FrM5 Surface Heterogeneity and Inhomogeneous Broadening of Vibrational Line Profiles**, *S. Taj, D. Baird, A. Rosu-Finsen,* ***Martin McCoustra***, Heriot-Watt University, UK

The surface heterogeneity of amorphous silica (aSiO$_2$) has been probed using coverage dependent temperature programmed desorption (TPD) of a simple probe molecule, carbon monoxide (CO). As a proof-of-principle, the resulting distribution of interaction energies is the foundation from which an environmentally broadened vibrational line profile synthesis has been undertaken. These simulations are compared with measured line profiles recorded at 0.1 cm$^{-1}$ resolution using reflection–absorption infrared spectroscopy (RAIRS). Additional demonstrations of this methodology on solid water and methanol surfaces will be reported.

10:20am **SS+HC-FrM7 Ab-Initio Study of Low Index Surface Planes of γ-Al2O3 and their Interface with Pt**, ***Kofi Oware Sarfo***, *A.L. Clauser, Z.L. McClure, M. Santala,* Oregon State University, *L. Árnadóttir*, Oregon State University

Metal/metal oxide interfaces are important because of their substantial impact on the composite properties of materials in a vast range of scientific and technological applications. Historically, metal oxides have been used as thermal barriers to protect metals from thermal degeneration in high temperature environments. Metal/oxide interfaces are important in applications such as protective coatings for metal medical implants, in electronic devices, and in heterogeneous catalysis mostly as catalyst support. γ-Al2O3 is a common catalyst support due to its high surface area, which enables fine dispersal of metal catalysts, such as Pt, Pd, Ru, and Rh. The structure and metal/metal oxide interactions at the interface of these materials can significantly impact the electronic and mechanical properties of the catalyst and the support. In this work, we combine theoretical and experimental approaches to study the nature of the metal/metal oxide interface between γ-Al2O3 and Pt. The theoretical approach utilized density functional theory (DFT) to study the structure and atomistic interactions at the interface. To determine the effect of the environment on the stability of different surface termination, we calculate the surface energy of three different low index planes and possible terminations of γ-Al2O3 as a function of partial pressures of oxygen at the experimental fabrication temperature (1100K). The (100) surface plane of γ-Al2O3 was found to be most stable and the (111) surface plane had the highest surface energy corresponding to lowest stability due to its highly polar structure. The stoichiometric terminations were found to be the most stable for the (100) and (110) planes at all partial pressures of oxygen, while the most stable termination of the (111) plane transitions from the stoichiometric surface to an oxygen rich surface termination at higher partial pressures of oxygen. This provides the basis for the experimental study of the atomic structure of the interface between γ-Al2O3 and Pt nanoparticles.

11:00am **SS+HC-FrM9 Ambient STM Study of Sequentially Adsorbed Octanethiol and Biphenylthiol Monolayers on Au(111)**, ***Gaby Avila-Bront***, College of the Holy Cross

The mixed monolayers of biphenyl-4-thiol (BPT) and octanethiol (OT) are studied at the molecular level using

scanning tunneling microscopy (STM) in ambient conditions and X-ray photoelectron spectroscopy (XPS) on

Au(111). The effect of both the sequence of deposition, and the concentration of the BPT solution used is

investigated. We observe signs of coexisting domains in the form of disordered patches surrounding flat patches

when a 100 µM solution of BPT is used. This observation holds for both OT being deposited first, and BPT being

deposited first. The most clear formation of coexisting domains occurs when an OT monolayer is immersed in a

100 µM solution of BPT. The XP spectra reveal a shift in the C 1s signal of the monolayers that is unique to what

films are deposited on the surface. These data demonstrate the importance characterizing mixed self-assembled

monolayers that form final monolayer structures unique to each mixture.

11:20am **SS+HC-FrM10 Molecule Assembly Structure and Tilt Geometry Evaluation of 5,6,7-Trithiapentacene-13-one (TTPO) / Pentacene-Quinone on Au(111) with NC-AFM**, *A. Larson,* University of New Hampshire, *P. Zahl,* Brookhaven National Laboratory, ***Karsten Pohl***, University of New Hampshire

Using non-contact atomic force microscopy (NC-AFM) the 3D molecular structure, tilt and assembly details of a new pentacene-based organic semiconductor, 5,6,7-trithiapentacene-13-one (TTPO) adsorbed on Au(111) were determined. 3D AFM force maps of individually resolved molecular orbitals were acquired to visualize the complete adsorption structure.

Robust, thermally stable, and highly inert to photo-oxidation, TTPO is a very promising organic semiconductor. Simple to synthesize and purify, TTPO readily crystallizes and is indefinitely stable against degradation in acid-free solution. TTPO has a high molar absorptivity, optical and electrochemical HOMO−LUMO gaps of 1.90 and 1.71 eV, respectively. Melting in air from 386−388°C without decomposition, TTPO can be thermally evaporated to produce highly uniform thin films. TTPO has the potential to be used in thin-film electronic devices that require operation over a wide range of temperatures such as transistors, switches, sensors, and solar cells. When adsorbed on a gold electrode, initial scanning tunneling microscopy (STM) experiments and first-principle computation reveal a novel 3-D angular assembly of the TTPO molecules, with the long axis of the molecule parallel to the gold surface, distinctive from any previously observed pentacene and pentacene derivative assemblies. Structures assembled are angularly dependent on TTPO molecular interactions, while commensurate with the underlying gold substrate, allowing for potential tailoring of pi-molecular orbital overlap through tilt-angle control. Understanding of the structure of these novel organic-metallic interfaces will guide nanoscale modifications for improved electrical transport and energy-conversion efficiency in future devices.

Single molecule STM images are input for DFT calculations to model the most-probable adsorption structure, in particular the molecular tilt-angle. NC-AFM, in contrast, is potentially the only technique capable of directly resolving the 3D angular arrangement of the individual adsorbed molecule. Indeed, by evaluating consecutively acquired constant height force maps, we were able to directly measure the 3D structure and tilt of small TTPO and Pentacene-Quinone byproduct assemblies on Au (111). Using GXSM-3, a new constant height mode “fuzzy-regulation” with current based compliance setting was used to scan a wider range of height’s otherwise not possible without losing the CO terminated tip molecule. Comparing 3D AFM force maps with a mechanical probe particle based simulation the molecule tilt was evaluated to 11±1°.

## Thin Films Division
## Room: 20 - Session TF-FrM

## Self-assembled Monolayers and Organic/Inorganic Interface Engineering
**Moderator:** Adrienne Stiff-Roberts, Duke University

8:20am **TF-FrM1 Kinetics of Swelling and Deswelling in Thermoresponsive Polymers Deposited by Initiated Chemical Vapor Deposition**, *P. Salzmann*, Graz University of Technology, *A. Perrotta*, Eindhoven University of Technology, Netherlands, ***AnnaMaria Coclite***, Graz University of Technology, Austria

Thermo-responsive polymers, like the Poly-(N Isopropylacrylamide) p(NIPAAm), change their properties (e.g. thickness and wettability) upon small changes in the environment temperature. This makes them suitable for interesting applications as smart sensors, artificial muscles or drug delivery systems. The change in the film properties arises from a coil to globule transition from a swollen hydrophilic state at temperatures below the lower critical solution temperature (LCST) to a shrunken hydrophobic state when the material is heated to temperatures higher than the LCST.

Cross-linked thin polymer films of NIPAAm were synthesized by initiated chemical vapor deposition (iCVD) and their thermoresponse was studied in-situ in water and in humidity by ellipsometry.

The film thicknesses were up to three times higher at temperatures below the LCST than at higher temperatures. Temperature cycles and different heating ramps revealed different mechanism of swelling and deswelling. The response during the cooling (i.e. during the swelling) was characterized by an LCST of 23°C. During the heating process (i.e. deswelling) the LCST was as high as 36°C. Similar discrepancies were also observed with another thermoresponsive polymer (N,N-Diethylacrylamide) deposited by iCVD. The reason was ascribed to different diffusion kinetics of water in the polymer meshes, and different arrangements of the polymer chains at the interface with water, depending on the rate of increase or decrease in temperature. A detailed investigation of these processes will be shown due to its importance for sensing applications.

9:40am **TF-FrM5 the Curious Wetting Behavior of ALD Grown $Al_2O_3$ Thin Film Surfaces**, ***Yi Li***, *B.D. Piercy, M.D. Losego*, Georgia Institute of Technology

**The curious wetting behavior of ALD grown $Al_2O_3$ thin film surfaces**

Yi Li, Brandon D. Piercy, Mark D. Losego

Conventional wisdom suggests that $Al_2O_3$ surfaces should be hydrophilic. Recently, it was demonstrated by the Parsons lab at NC State that under certain conditions a few cycles of trimethylaluminum-water atomic layer deposition (ALD) transforms cotton fiber surfaces from hydrophilic to hydrophobic. These researchers suggest that adventitious carbon from ambient atmosphere is the source of this hydrophobicity, but they make no note of the universality of this phenomenon. In our effort to better understand this phenomenon, we discovered that ALD grown $Al_2O_3$ thin films of “any” thickness (1 nm to >50 nm) on “any” substrate (including silicon) can be transformed into a relatively hydrophobic surface state (water contact angles > 80°) when heat treated under appropriate conditions. After heat treatment, ellipsometry detects several angstroms increase in thickness and XPS suggests this layer is some form of hydrocarbon. In this talk, we will discuss our evaluation of three hypotheses for the source of this hydrocarbon layer: (1) contamination from the heating environment (e.g., oven), (2) carbon contamination from the ALD deposition process (i.e., unpyrolized ligands), and (3) adventitious carbon from the atmosphere. To address hypotheses (1) and (3), $Al_2O_3$ thin films grown by ALD to 10 nm thickness on silicon are found to become hydrophobic if we remove them from the ALD reactor and then re-anneal them in either a “dirty” ambient air oven or the “clean” ALD reactor under low-pressure and ultra-pure flowing nitrogen conditions. To further verify the purity of the ALD reactor, we have done this annealing step without breaking vacuum in the ALD reactor, leading to the $Al_2O_3$ surface remaining hydrophilic. Films annealed to 700 °C for 4 hours to fully pyrolyzed any remaining organics (still hydrophilic) and then re-heated to 150 °C for 30 min are also found to turn hydrophobic, suggesting that residual carbon within the film is also not the source. Thus, we believe that the $Al_2O_3$ surface is attracting adventitious carbon from ambient atmosphere and then reacting with the surface to form a hydrophobic layer. This reaction, which is thermally accelerated, appears to be key to the transition. We will report on how both temperature and time affect this surface reaction and our best understanding of the surface chemistry based on various surface spectroscopy techniques.

10:00am **TF-FrM6 Controlled Thicknesses of Vapor Deposited Silane Films**, ***Brian Johnson***, *A. Diwan, M.R. Linford*, Brigham Young University

Solution-based silane deposition is well known and has been widely studied. Increasingly, however, people are recognizing the importance of vapor phase deposition of these important reagents. Indeed, these gas phase depositions can be highly reproducible, they involve no solvent, and they can be integrated into production processes. Some of their disadvantages are the cost of the vacuum equipment/ovens needed, and the limitations inherent to the vapor phase, e.g., one cannot allow a polymerization of a silane to take place before the reagent/polymer is deposited on a surface as one can in a solution phase deposition. In this presentation we describe processes for controlling and increasing thicknesses of silane films on silicon surfaces. Variables studied in this work include process temperature, pressure, and reagent concentration. Silane films have been characterized by X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), spectroscopic ellipsometry (SE), and wetting. The depositions described in this work were performed in a commercial chemical vapor deposition (CVD) oven (the 1224P by Yield Engineering Systems). Special emphasis in these studies was placed on minimizing carryover between runs.

10:20am **TF-FrM7 Supramolecular Heterostructures formed by Sequential Epitaxial Deposition of Two-Dimensional Hydrogen-Bonded Arrays**, *V.V. Korolkov, M. Baldoni*, The University of Nottingham, UK, *K. Watanabe, T. Taniguchi*, National Institute for Materials Science, Japan, *E. Besley*, ***Peter Beton***, The University of Nottingham, UK

The formation of two-dimensional supramolecular arrays provides a highly flexible route to the control of the spatial organization, down to the molecular scale, of the chemical functionality of a surface. These molecular networks, which can be formed through self-assembly processes on a variety of different substrates including semiconductors, metals, insulators[0] and layered materials, are, in almost all cases, limited to monolayer thickness. Progress towards the growth of higher layers has so far been much more limited, with demonstrations of bilayer growth and site-specific molecular adsorption. Specifically, the additional functional control, which may be achieved through the formation of heterostructures realized by placing one supramolecular layer on another and resulting in growth into the third dimension perpendicular to the substrate, has not been widely explored for these materials. Such additional control of material properties is well established for semiconductors, both organic and inorganic, and, more recently, layered materials, providing a strong motivation to explore analogue materials derived from stacked supramolecular networks. Here we describe the successful formation of heterostructures formed by the sequential growth of distinct one- and two-dimensional arrays. It is possible, using high resolution atomic force microscopy (AFM) to determine an epitaxial alignment between successive layers. Furthermore, we demonstrate using classical molecular dynamics (MD) simulations that the placement and dimensions of the layers may be robustly predicted using well established force-fields.

Supramolecular heterostructures[1] are formed by growing sequential layers of bi- and mono-component two-dimensional molecular arrays stabilized by hydrogen bonding. The heterostructures are formed on hexagonal boron nitride by depositing cyanuric acid/melamine (CA.M) followed by terephthalic acid (TPA) or trimesic acid (TMA) and imaged using atomic force microscopy under ambient conditions with resolution approaching 0.1 nm. A clear epitaxial arrangement is observed between these layers having intrinsically distinct symmetries and lattice constants, which for TMA/CA.M corresponds to a $(\sqrt{3}\ x\ \sqrt{3})R30^{o}$ phase, while TPA forms rows with a molecular separation that matches the CA.M period. Structures calculated using classical molecular dynamics are in excellent agreement with the orientation, registry and dimensions of the epitaxial layers. Calculations confirm that van der Waals interactions provide the dominant contribution to the adsorption energy and registry of the layers.

[1] Korolkov et al., Nat. Chem., 2017, in press.

10:40am **TF-FrM8 Functionalization and Stabilization of Ultrathin Alumina Films with Rhenium Photosensitizers**, ***Wolf-Dietrich Zabka***, *D. Leuenberger*, Department of Physics, University of Zürich, Switzerland, *G. Mette*, University of Zürich, Switzerland, *C. Monney*, University of Zürich, Switzerland, *M. Mosberger*, University of Zürich, Switzerland, *B. Probst-Rüd*, University of Zürich, Switzerland, *R. Alberto, J. Osterwalder*, University of Zürich, Switzerland

Ultrathin (ut) oxide films with a thickness of few atomic layers are often used as model systems for oxide surfaces and their interaction with adatoms, particles and molecules. In particular, epitaxial ut-alumina films grown on NiAl alloys have been used to study a wide range of phenomena under UHV-conditions [1,2]. However, their instability under ambient conditions limits the possibilities for application [3,4].

We developed a new wet chemistry setup directly attached to an existing ultra-high vacuum system that enables us to deposit self-assembled monolayers (SAM) from highly purified solvents onto substrates prepared under UHV conditions without exposure to air. The setup, the procedure for SAM-deposition and the characterization of residual contamination detected with X-ray photoelectron spectroscopy (XPS) will be described. Rhenium photosensitizers functionalized with carboxyl groups ($Re(CO)_3(NCS)$bipycarb) are attached onto ut-alumina films. XPS measurements indicate that the resulting structure is stable in air. First results from time-resolved photoemission spectroscopy suggest that by altering the oxide thickness, a variation of the lifetime of excited electrons can be achieved. Both, the substrate stabilization and the control of hot electron lifetimes offer new prospects for the application of such ultrathin oxide films involving charge transfer and related mechanisms.

[1] N. Nilius, Surf. Sci. Rep. 64, 595 (2009).

[2] U. Diebold, S. C. Li, and M. Schmid, Annu. Rev. Phys. Chem. 61, 129 (2010).

[3] A. Shavorskiy, K. Müller, J. T. Newberg, D. E. Starr, and H. Bluhm, J. Phys. Chem. C 118, 29340 (2014).

[4] J. Evertsson, F. Bertram, F. Zhang, L. Rullik, L. R. Merte, M. Shipilin, M. Soldemo, S. Ahmadie, N. Vinogradov, F. Carlà, J. Weissenrieder, M. Göthelid, J. Pan, A. Mikkelsen, J.-O. Nilsson, and E. Lundgren, Appl. Surf. Sci. 349, 826 (2015).

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