Monday Morning, October 30, 2017

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.

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

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

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

[3] O.E. Dagdeviren et al, Physical Review B, 93, 195303 (2016)

[4] O.E. Dagdeviren et al, Advanced Materials and Interfaces, 4, 1601011 (2017)

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].

Support by the European Commission under PAMS project (contract no. 610446) and by the Polish Ministry of Science and Higher Education (contract no. 0341/IP3/2016/74) are gratefully acknowledged.

[1] J. Yang et al., Eur. Phys. J. Appl. Phys., **73**, 10702 (2016)

[2] M. Kolmer et. al., Angew. Chem. Int. Ed., **52**, 10300 – 10303 (2013)

[3] M. Kolmer et. al., Chem. Comm., **51**, 11276 – 11279 (2015)

[4] G. Vasseur et al., J. Am. Chem. Soc., **138**, 5685−5692 (2016)

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 $\sqrt{3}$ 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.

References

[1] - Z. H. Xiong, D. Wu, Z. V. Vardeny, and J. Shi, *Nature***427**, 821 (2004).

[2] - P. P. Ruden, *Nat. Mater.***10**, 8 (2011).

[3] - T. S. Santos, J. S. Lee, P. Migdal, I. C. Lekshmi, B. Satpati, and J. S. Moodera, *Phys. Rev. Lett.* 98, 016601 (2007)

[4] - M. Gobbi, F. Golmar, R. Llopis, F. Casanova, Fèlix, and L. E. Hueso, *Adv. Mater.***23**, 1609 (2011).

[5] - X. Zhang, S. Mizukami, T. Kubota, Q. Ma, M. Oogane, H. Naganuma, Y. Ando, and T. Miyazaki, *Nat. Comm.***4**, 1392 (2013).

[6] - C. Boehme, J. M. Lupton, Nat. Nano. **8**, 612 (2013).

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.

[1] K. Werner, S. Mohr, M. Schwarz, T. Xu, M. Amende, T. Döpper, A. Görling, J. Libuda, Journal of Physical Chemistry Letters 7, 555 (2016)

[2] T. Xu, M. Schwarz, K. Werner, S. Mohr, M. Amende, J. Libuda, Chemistry - A European Journal 15, 5384 (2016)

[3] T. Xu, M. Schwarz, K. Werner, S. Mohr, M. Amende, J. Libuda, Physical Chemistry Chemical Physics 18, 10419 (2016)

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

[1] Ossowski, J; Wächter, T.; Silies, L.; Kind, M.; Noworolska, A.; Blobner, F.; Gnatek, D.; Rysz, J.; Bolte, M.; Feulner, P.; Terfort*, A.; Cyganik*, P.; Zharnikov*, M., *ACS Nano*, *Thiolate versus Selenolate: Structure, Stability and Charge Transfer Properties*, **9**, 4508-4526 (2015).

[2] Ossowski J. *et al* paper in preparation.

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).

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$_3$O$_4$, In$_2$O$_3$, 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 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

---

* **Coburn & Winters Student Award Finalist**

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 °C 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).

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).

1. Oehrlein, G. S. et al. *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.***29,** 10801 (2011).

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.

[1] K. Ishikawa et al., J. Appl. Phys. **104** (2008) 063306.

[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 (η_2-ketone diolate) formed by interaction with O-adatoms, whereas the η_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]

[1] D. F. Ogletree, H. Bluhm, E. D. Hebenstreit, and M. Salmeron. *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, 601, 1–2, 151–160, 2009.

[2] S. Pletincx, L. Trotochaud, L. Fockaert, J.M.C Mol, A. Head, O. Karslıoğlu, H. Bluhm, H. Terryn, T. Hauffman. *Sci. Rep.7* (45123), 2017.

[3] M. Öhman and D. Persson, *Surf. Interface Anal.,* 44, 2, 133–143, 2012.

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.

1. NIST Electron Effective-Attenuation-Length Database, SRD 82, Version 1.3, 2011; https://www.nist.gov/srd/nist-standard-reference-database-82.
2. A. Jablonski and C. J. Powell, J. Electron Spectrosc. Relat. Phenom. 199, 27 (2015).
3. A. Jablonski, J. Electron Spectrosc. Relat. Phenom. 185, 498 (2012).
4. A. Jablonski and C. J. Powell (to be published).
5. C. J. Powell, W. S. M. Werner, A. G. Shard, and D. G. Castner, J. Phys. Chem. C 120, 22730 (2016).
6. A. Jablonski (to be published).

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.

[1] Niehuis et al., Surface and Interface Analysis, 45, 158-162, 2013

[2] Shard et al., Analytical Chemistry, 84, 7865-73, 2012

[3] Shard et al., International Journal of Mass Spectrometry, 377, 599-609, 2015

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, σ (1), corrected for transmission function, T, and escape depth, λ.

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

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

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

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

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

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

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

3 P. S. Baguset al., J. Chem. Phys., in press (2017).

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.

1. S. A. Chambers, in Hard X-Ray Photoelectron Spectroscopy (HAXPES), edited by J. C. Woicik (Springer, Heidelberg, 2016), Vol. 59, p. 341

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)

4. R. Manne and T. Åberg, Chem. Phys. Lett. , 282 (1970)

5. P. S. Bagus, E. S. Ilton, and C. J. Nelin, Surf. Sci. Rep. , 273 (2013)

6. M. Taguchi, T. Uozumi, and A. Kotani, J. Phys. Soc. Jpn. , 247 (1997)

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+}.

References

1. Bravo Sanchez, M., Huerta-Ruelas, J. A., Cabrera-German, D. & Herrera-Gomez, A. Composition assessment of ferric oxide by accurate peak fitting of the Fe 2p photoemission spectrum. *Surf. Interface Anal.* (2016). doi:10.1002/sia.6124

2. Cabrera-German, D., Gomez-Sosa, G. & Herrera-Gomez, A. Accurate peak fitting and subsequent quantitative composition analysis of the spectrum of Co 2p obtained with Al K α radiation: I: cobalt spinel. *Surf. Interface Anal.***48,** 252–256 (2016).

3. Herrera-Gomez, A., Bravo-Sanchez, M., Ceballos-Sanchez, O. & Vazquez-Lepe, M. O. Practical methods for background subtraction in photoemission spectra. *Surf. Interface Anal.***46,** 897–905 (2014).

4. Pauly, N., Tougaard, S. & Yubero, F. Determination of the Cu 2p primary excitation spectra for Cu, Cu 2O and CuO. *Surf. Sci.***620,** 17–22 (2014).

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.

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.

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.

[1] M.C. Biesinger, L.W.M. Lau, A.R. Gerson, R.S.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn, Appl. Surf. Sci. 257 (2010) 887–898.

[2] J. Végh, The analytical form of the Shirley-type background, J. Electron Spectros . Relat. Phenomena. 46 (1988) 411–417.

[3] A.M. Salvi, J.E. Castle, The intrinsic asymmetry of photoelectron peaks: dependence on chemical state and role in curve fitting., J. Electron Spectros . Relat. Phenomena. 95 (1998) 45–56.

[4] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, M.O. Vazquez-Lepe, Practical methods for background subtraction in photoemission spectra, Surf. Interface Anal. 46 (2014) 897–905.

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 μ_B, which is highly localised on the transition metal.

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

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 (ν_d) is imparted to the free carriers. If the drift velocity is slower than (or opposite to) the acoustic wave velocity (ν_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.

[1] J. H. McFee, “Transmission and Amplification of Acoustic Waves in Piezoelectric Semiconductors," Phys. Acous. A, vol. 4, 1-45 (1966).

[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.

[1] J. T. Muhonen et al., Nature Nanotechnology 9, 986 (2014).

[2] B.E. Kane, Nature 393, 133 (1998).

[3] M. Fuechsle et al., Nature Nanotechnology 7, 242 (2012).

[4] B. Weber et al., Science 335, 6064 (2012).

[5] H. Buch et al., Nature Communications 4, 2017 (2013).

[6] T.F. Watson et al., Physical Review Letters 115, 166806 (2015).

[7] S. Shamim et al., Nano Letters 16, 5779 (2016).

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.

1. A. J. Mannix, X.-F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, B. D. Myers, X. Liu, B. L. Fisher, U. Santiago, J. R. Guest, M. J. Yacaman, A. Ponce, A. R. Oganov, M. C. Hersam, N. P. Guisinger, *Science***350**, 1513–1516 (2015).

2. B. Feng, J. Zhang, Q. Zhong, W. Li, S. Li, H. Li, P. Cheng, S. Meng, L. Chen, K. Wu, *Nat. Chem.***8**, 563–568 (2016).

*** NSTD Student Award Finalist**

3. Y. Liu, E. S. Penev, B. I. Yakobson, *Angew. Chem. Int. Ed.***52**, 3156–3159 (2013).

4. X. Liu, Z. Wei, I. Balla, A. J. Mannix, N. P. Guisinger, E. Luijten, and M. C. Hersam, *Sci. Adv*. **3**, e1602356 (2017).

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.

[1] H. Bhaskaran *et al*. Appl. Phys. Lett. **98**, 013502 (2011).

[2] L. Liu *et al*., Phys. Rev. Lett. **106**, 036601 (2011).

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).

References

[1] H.-Y. Hui *et al.*, Sci. Rep.. **5**, 8880 (2015).

[2] J. Alicea *et al.*, Nature Phys. **7**, 412 (2011).

[3] S. Nadj-Perge *et al.*, Science **346**, 602 (2014).

[4] M. Ruby *et al.*, Phys. Rev. Lett. **115**, 197204 (2015).

[5] R. Pawlak *et al.*, NPJ Quantum Information **2**, 16035 (2016).

[6] B. E. Feldman *et al.*, Nature Phys. **13**, 286 (2017).

[7] M. Menzel *et al.*, Phys. Rev. Lett. **108**, 197204 (2012).

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.

References:

[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

---

* **Morton S. Traum Award Finalist**

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)

References:

(1) Fan, Q.; Wang, C.; et al., *Angew. Chem. Int. Ed.***2013**, *52*, 4668.

(2) Fan, Q.; Wang, C.; et al., *ACS Nano***2014**, *8*, 709.

(3) Dai, J.; Fan, Q.; et al., *Phys. Chem. Chem. Phys.***2016**, *18*, 20627.

(4) Fan, Q.; Dai, J.; et al., *ACS Nano***2016**, *10*, 3747.

(5) Fan, Q.; Wang, T.; et al., *ACS Nano***2017,** DOI: 10.1021/acsnano.7b01870.

(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 1×10^{-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).

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.

[1] – Acc. Chem. Res. 46(8), pp.1740-1748.

[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 π-π 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.

---

* **Morton S. Traum Award Finalist**

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.

References

[1] Zhuang, J.-L.; Terfort, A.; Wöll, C. *Coord. Chem. Rev.* 307 (**2016**) 391-424.

[2] Zhuang, J.-L.; Kind, M.; Grytz, C. M.; Farr, F.; Diefenbach,M.; Tussupbayev, S.; Holthausen, M. C.; Terfort, A. *J. Am. Chem. Soc.* 137 (**2015**) 8237-8243.

[3] Yu, X.-J.; Zhuang, J.-L.; Scherr,J.; Abu-Husein,T.; Terfort, A. *Angew. Chem. Int. Ed.* 29 (**2016**) 8348-8352.

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.

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 $cm^2V^{-1}s^{-1}$. 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.

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, γ^T, since this property can be modeled by Van Oss theory, to consist of three component interaction energies: molecular dipoles (Lifschitz-Van der Waals), γ^{LW}, electron donors, γ^-, and electron acceptors, γ^+. 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 γ^{LW}. In hydrophobic oxide surfaces, γ^T is due almost entirely to molecular interactions, γ^{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 γ^{LW}. However, γ^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 γ^+, raises the total surface energy γ^T up to 40% above that of γ^{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 γ^{LW}contributing 98 ± 2%, thus close to the entirety of γ^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 x 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.

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→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$_2$O. 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.

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.

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 ≈ 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]

[1] H.F. Winters and J.W. Coburn, "Surface science aspects of etching reactions," Surf. Sci. Rep. 14, 161 (1992)

[2] D. Metzler, R. Bruce, S. Engelmann, E. A. Joseph, and G. S. Oehrlein, "Fluorocarbon assisted atomic layer etching of SiO_2 using cyclic Ar/ C_4F_8 plasma", J. Vac. Sci. Technol. A **32**, 020603 (2014).

[3] E. A. J. Bartis, A. J. Knoll, P. Luan, J. Seog, and G. S. Oehrlein, "On the Interaction of Cold Atmospheric Pressure Plasma with Surfaces of Bio-molecules and Model Polymers", Plasma Chemistry and Plasma Processing **36**, 121 (2016); P. Luan, A. J. Knoll, H. Wang, V. S. S. K. Kondeti, P. J. Bruggeman, and G. S. Oehrlein, "Model polymer etching and surface modification by a time modulated RF plasma jet: role of atomic oxygen and water vapor," Journal of Physics D-Applied Physics **50**, 03LT02 (2017).

* 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.

F. Maier, I. Niedermaier, and H.-P. Steinrück, *"Perspective: Chemical Reactions in Ionic Liquids Monitored through the Gas (Vacuum)/Liquid Interface"*, J.Chem. Phys. **2017** (in press)

H.-P. Steinrück and P. Wasserscheid, "*Ionic Liquids in Catalysis*", Catal. Lett. **2015**, *145*, 380.

H.-P. Steinrück, "*Recent developments in the study of ionic liquid interfaces using X-ray photoelectron spectroscopy and potential future directions*", Phys. Chem. Chem. Phys. **2012**, *14*, 2510.

H.-P. Steinrück, "*Surface Science goes liquid !*", Surf. Sci. **2010**, *604*, 481.

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.

[1] E. Lind *et al.,* IEEE J. El. Dev. Soc. **3**, 96 (2015).

[2] J. Wallentin *et al*., Science **339**, 1057 (2013).

[3] R. Timm *et al*., Appl. Phys. Lett. **99**, 222907 (2011); J. Webb *et al.*, Nano Lett. **15**, 4865 (2015).

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

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,

---

* **Medard W. Welch Award Winner**

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 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

1. Kozicki MN, Barnaby HJ. Conductive bridging random access memory—materials, devices and applications. Semicond Sci Technol. 2016;31(11):113001.

2. Waser R, Dittmann R, Staikov G, Szot K. Redox-Based Resistive Switching Memories - Nanoionic Mechanisms, Prospects, and Challenges. Adv Mater. 2009 Jul 13;21(25-26):2632–63.

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 to a deeper understanding of the fundamental effects that govern how materials interact with their surroundings at sub-nanometer scale. Entangling these fundamental principles with design will enable fabrication and synthesis of better nanodevices with graphene and other layered materials as well as nanotubes.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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.

*** NSTD Student Award Finalist**

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.

References:

[1] I. Amenabar et al., Nature Comm. 8, 14402 (2017)

[2] J. M. Stiegler et al., Nano Lett. 10, 1387 (2010)

[3] J. Chen et al., Nature 487, 77 (2012)

[4] Z. Fei et al., Nature 487, 82 (2012)

[5] E. Yoxall et al., Nature Photon. 9, 674 (2015)

[6] F. Hu et al., Nature Photon. 11, 356 (2017)

[7] M. Wagner et al., Nano Lett. 14, 894 (2014)

[8] M. Eisele et al., Nature Photon. 8, 841 (2014)

[9] M. Huber et al., Nature Nanotech. 12, 207 (2017)

[10] G. X. Ni et al., Nature Photon. 10, 244 (2016)

[11] A. S. McLeod et al., Nature Phys. 13, 80 (2017)

[12] www.neaspec.com

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

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

5:40pm **SP+AS+MI+NS+SS-TuA11 Breaking the Time Barrier in Scanning Probe Force Microscopy: Fast Free Force Reconstruction (F^{3}R) 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^{3}R)[1] utilizing big data capture and analytics. F^{3}R-AFM is based on the G-mode acquisition platform [2] and allows direct reconstruction of the tip-sample forces with much higher time resolution (~µs) than possible using standard AFM detection methods (~ms). We describe how fast data acquisition, coupled with multivariate statistical denoising methods can be harnessed to overcome the widely viewed temporal bottleneck in AFM, the mechanical bandwidth of the cantilever. Finally, we will demonstrate quantitative recovery of tip-sample forces with <10 µs time resolution, free from influences of the cantilever ring-down as well as discussing the fundamentally time and information limits of the approach.

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

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

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

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

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

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

[1] Collins, Liam, et al. "Multifrequency spectrum analysis using fully digital G Mode-Kelvin probe force microscopy." *Nanotechnology* 27.10 (2016): 105706.

[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.

[3] Collins, Liam, et al. "Breaking the Time Barrier in Kelvin Probe Force Microscopy: Fast Free Force Reconstruction Using the G-Mode Platform." *ACS nano* (2017).

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 $\sqrt{5}$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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-$_2$O 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

---

* **Morton S. Traum Award Finalist**

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 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 $\sim 8.65\times10^{-14}$ kg/s. This is significantly smaller than the theoretically-predicted value of 2.0×10^{-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)

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 ($\leq$ 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.

[1] A. Turchanin and A. Gölzhäuser, Carbon Nanomembranes, *Adv. Mater.* 28 (2016) 5075

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.

[1] S. Ninomiya, K. Ichiki, H. Yamada, Y. Nakata, T. Seki, T. Aoki, J. Matsuo, Rapid Commun. Mass Spectrom. 23, 2009, 1601.

[2] M. P. Seah, The Journal of Physical Chemistry C 117(24), 2013, 12622.

[3] B. Czerwinski, L. Rzeznik, R. Paruch, B. J. Garrison, Z. Postawa, Nucl. Instrum. Meth. Phys. Res. Sect. B 269, 2011, 1578.

[4] A. Delcorte, M. Debongnie, J. Phys. Chem. C 119, 2015, 25868.

[5] K. Mochiji, N. Se, N. Inui, K. Moritani, Rapid Commun. Mass Spectrom. 28, 2014, 2141.

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.

[1] A.D. Appelhans, et. al., Anal. Chem. 59 (13) (1987) 1685–1691

[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

---

* **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.

1) K. Wittmaack, *Surface Science Reports*, 68 (2013) 108-230.

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.

4) J. Brison, R. Hubert, S. Lucas and L. Houssiau, *Surf. Interface Anal*. 2006; 38: 1654-1657.

Sandia National Laboratories is a multimission 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.

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.

References

[1] J.-G. Wang, X. Cao, X. Wang, S. Yang, R. Wang, Electrochim. Acta 2014, 138, 174.

[2] J.-G. Wang, J. S. Fossey, M. Li, D.-W. Li, W. Ma, Y.-L. Ying, R.-C. Qian, C. Cao, Y.-T. Long, J. Electroanal. Chem. 2016, 781, 257.

[3] J.-G. Wang, C. Jing, Y.-T. Long, in Frontiers of Plasmon Enhanced Spectroscopy Volume 2, Vol. 1246, American Chemical Society, 2016, pp. 57.

[4] J. T. Cox, B. Zhang, Annu. Rev. Anal. Chem. 2012, 5, 253.

[5] T. A. Brown, H. Chen, R. N. Zare, J. Am. Chem. Soc. 2015, 137, 7274.

[6] Z. Wang, Y. Zhang, B. Liu, K. Wu, S. Thevuthasan, D. R. Baer, Z. Zhu, X.-Y. Yu, F. Wang, Anal. Chem. 2017, 89, 960.

[7] D. C. Dahlin, G. T. Miwa, A. Y. Lu, S. D. Nelson, Proc. Natl. Acad. Sci. 1984, 81, 1327.

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.

References:

(1) Feng, X.; Jiang, K.; Fan, S.; Kanan, M. W. *J. Am. Chem. Soc.***2015**, *137*, 4606–4609.

(2) Feng, X.; Jiang, K.; Fan, S.; Kanan, M. W. *ACS Cent. Sci.***2016**, *2*, 169−174.

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.*

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 experimental 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$_{3\text{-}x}$Cl$_x$, I$_{3\text{-}x}$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$_2$O$_3$) 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.

Acknowledgement

"Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. The abstract has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government. Office of Science User Facility under Contract No. DE-AC02-06CH11357. M.A. also acknowledges support from the Joseph Katz Named Fellowship at Argonne National Laboratory."

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, ρ, and thereby induce a transition from variable range hopping to metallic transport. We determine n from the NCs' localized surface plasmon resonance (LSPR) and ρ 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.

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.

---

* **Coburn & Winters Student Award Finalist**

[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.

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].

References:

1. Ritter, K.; Lyding, J., The influence of edge structure on the electronic properties of graphene quantum dots and nanoribbons. *Nature Materials* **2009,***8* (3), 235-242.

2. Ruppalt, L.; Lyding, J., Charge transfer between semiconducting carbon nanotubes and their doped GaAs(110) and InAs(110) substrates detected by scanning tunnelling spectroscopy. *Nanotechnology* **2007,***18* (21).

3. Radocea, A.; Sun, T.; Vo, T.; Sinitskii, A.; Aluru, N.; Lyding, J., Solution-Synthesized Chevron Graphene Nanoribbons Exfoliated onto H:Si(100). *Nano Letters* **2017,***17* (1), 170-178.

4. Ye, W.; Martin, P. A. P.; Kumar, N.; Daly, S. R.; Rockett, A. A.; Abelson, J. R.; Girolami, G. S.; Lyding, J. W., Direct Writing of Sub-5 nm Hafnium Diboride Metallic Nanostructures. *Acs Nano* **2010,***4* (11), 6818-6824.

5. Schmucker, S.; Kumar, N.; Abelson, J.; Daly, S.; Girolami, G.; Bischof, M.; Jaeger, D.; Reidy, R.; Gorman, B.; Alexander, J.; Ballard, J.; Randall, J.; Lyding, J., Field-directed sputter sharpening for tailored probe materials and atomic-scale lithography. *Nature Communications* **2012,***3*.

6. Do, J.; Estrada, D.; Xie, X.; Chang, N.; Mallek, J.; Girolami, G.; Rogers, J.; Pop, E.; Lyding, J., Nanosoldering Carbon Nanotube Junctions by Local Chemical Vapor Deposition for Improved Device Performance. *Nano Letters* **2013,***13* (12), 5844-5850.

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 . They 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.

1. Marder, Michael, Tadeusz Patzek, and Scott W. Tinker. "Physics, fracking, fuel, and the future." *Physics Today* 69.7 (2016): 46-52.

2. Lake, Larry W. "Enhanced oil recovery." (1989): 17-39.

3. *Key world energy statistics*. International Energy Agency: 2016, https://www.iea.org/

4. Berlin, Jacob M., et al. "Engineered nanoparticles for hydrocarbon detection in oil-field rocks." *Energy & Environmental Science* 4.2 (2011): 505-509.

5. S.L. Eichmann and N.A. Burnham, "Calcium-Mediated Adhesion of Nanomaterials in Reservoir Fluids." submitted.

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.

References

1. Castellanos-Gomez, A.; Poot, M.; Amor-Amorós, A.; Steele, G. A.; van der Zant, H. S. J.; Agraït, N.; Rubio-Bollinger, G., Mechanical properties of freely suspended atomically thin dielectric layers of mica. Nano Research 2012, 5 (8), 550-557.

2. Lu, X. F.; Majewski, L. A.; Song, A. M., Electrical characterization of mica as an insulator for organic field-effect transistors. Organic Electronics 2008, 9 (4), 473-480.

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

1.M. Hupalo et al *Advanc. Mater.* 23 2082 (2011) 2.X. Liu, et al. *Progr. Surf. Sci.* 90 397 (2015) 3. D. Mc Dougall et al *Carbon* 108 283 (2016)) 4. X. Liu et al. *Nano Research* 9(5): 1434 (2016)

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_2O_3 film on $Ni_3Al(111)$ [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.

---

[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_2O. 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.

[1] S.Y. Tong “Surface Crystallography by LEED: Theory, Computation, and Structural Results”, Springer.

[2] H.L. Davis et al , Phys. Rev. Lett. 68, 2632 (1992).

[3] V. Chis and B. Hellsing, Phys. Rev. Lett. 93, 226103 (2004).

[4] F. Reinert et al, Phys. Rev. B 63, 115415 (2001).

[5] J. Sun et al, New Journal of Phys. 12, 063016 (2010).

[6] Li Guan et al, Solid. State. Commun. 149, 1561 (2009).

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 ºC on a 500 µm thick silicon wafer with an initial temperature of 22ºC. 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 ºC 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.

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.

[1] T.Wadayama et al., Electrochem.Commun. **12**, 1112 (2010). N.Todoroki et al., PCCP, **15**, 17771 (2013). M.Asano et al., ACS catal. **6**, 5285 (2016).

[2] S. Takahashi et al., PCCP, **17**, 18638 (2015). S. Takahashi et al., ACS Omega **1**, 1247 (2016).

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 5.0×10^{-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.

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-

---

* **Morton S. Traum Award Finalist**

† **NSTD Student Award Finalist**

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 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.

Research sponsored by US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division; and 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. DFT calculations were supported by DOE Grant No. DE-FG02-09ER46554.

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

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 2×10^{-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

---

* **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.

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.

References

1. D. E. Starr et.al, Chemical Society reviews 42, 5833-57 (2013).

2. S. Axnanda et. al, Scientific Reports, 5,9788 (2015).

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

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.

Reference

1. J. D. Stoll and A. Kolmakov, Nanotechnology 23 (50), 505704 (2012).

2. A. Kolmakov, D. A. Dikin, L. J. Cote, J. Huang, M. K. Abyaneh, M. Amati, L. Gregoratti, S. Günther and M. Kiskinova, Nature nanotechnology 6 (10), 651-657 (2011).

3. H. Guo, E. Strelcov, A. Yulaev, J. Wang, N. Appathurai, S. Urquhart, J. Vinson, S. Sahu, M. Zwolak and A. Kolmakov, Nano letters (2017).

4. J. Kraus, R. Reichelt, S. Günther, L. Gregoratti, M. Amati, M. Kiskinova, A. Yulaev, I. Vlassiouk and A. Kolmakov, Nanoscale 6 (23), 14394-14403 (2014).

5. R. S. Weatherup, B. Eren, Y. Hao, H. Bluhm and M. B. Salmeron, The journal of physical chemistry letters 7 (9), 1622-1627 (2016).

6. J.-J. Velasco-Velez, C. H. Wu, T. A. Pascal, L. F. Wan, J. Guo, D. Prendergast and M. Salmeron, Science 346 (6211), 831-834 (2014).

7. A. Yulaev, H. Guo, E. Strelcov, L. Chen, I. Vlassiokiv and A. Kolmakov, ACS Applied Materials & Interfaces (accepted) (2017).

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.

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.

[1] R. Waser and M. Aono, Nat. Mater. **6**, 833 (2007).

[2] R. Waser, R. Dittmann, G. Staikov, and K. Szot, Adv. Mater. **21**, 2632 (2009).

[3] C. Baeumer, C. Schmitz, A. Marchewka, D. N. Mueller, R. Valenta, J. Hackl, N. Raab, S. P. Rogers, M. I. Khan, S. Nemsak, M. Shim, S. Menzel, C. M. Schneider, R. Waser, and R. Dittmann, Nat. Commun. **7**, 12398 (2016).

[4] C. Baeumer, C. Schmitz, A. H. H. Ramadan, H. Du, K. Skaja, V. Feyer, P. Muller, B. Arndt, C. Jia, J. Mayer, R. A. De Souza, C. Michael Schneider, R. Waser, and R. Dittmann, Nat. Commun. **6**, 9610 (2015).

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.

[1] X.Z. Yu et al., Nature 465, 901 (2010). [2] N. Romming et al., Science 341, 636 (2013). [3] A. Fert, V. Cros & J. Sampaio, Nature Nanotech. 8, 152 (2013). [4] O. Boulle, J. Vogel et al., Nature Nanotech. 11, 449 (2016).

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)2×1 surfaces were oxidized at 400°C under the O_2 pressure of 3.2×10^{-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 6.4×10^{-5} Pa to 3.2×10^{-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 1.5×10^{-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].

[1] H.Y.A. Chung, *et al*., Mater. Sci. Eng. B, **118,** 55 (2005).

[2] S. Ogawa *et al*., J. Chem. Phys., **145,** 114701 (2016).

[3] S. Ogawa *et al*., Jpn. J. Appl. Phys., **46,** 7063 (2006).

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.

[1] A. Hexemer, P. Müller-Buschbaum, IUCrJ 2, 106-125 (2015)

[2] A. Buffet, et al., J. Synchrotron Radiat., 19(4), 647-653 (2012)

[3] G. Benecke, et al., J. Appl. Crystallogr., 47(5), 1797-1803 (2014)

[4] M. Schwartzkopf et al., ACS Appl. Mater. Interfaces, 7(24), 13547-13556 (2015)

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 $Zr/Al_2O_3(0001)$: Effect of Substrate Temperature on Zr Thin Film Microstructure and Thermal Stability of Zr-Al_2O_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 ≤ T_s < 750 ºC, we obtain fully dense, hexagonal close-packed structured Zr(0001) thin films with smooth surfaces. At T_s ≥ 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_2O_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 ($\mu \sim 0.2\text{-}0.3$) 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).

[2] Y. Zhang, H. Kersell, R. Stefak, J. Echeverria, V. Iancu, U. G. E. Perera, Y. Li, A. Deshpande, K.-F. Braun, C. Joachim, G. Rapenne, and S.-W. Hla. ***Nature Nanotechnology* 11**, 706-711 (2016).

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)
2. K. L. Man et al., Phys. Rev. Lett. 110, 036104 (2013)
3. C. H. Mullet et al., manuscript submitted.
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.

---

* **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.

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

---

*** ASSD Student Award Finalist**

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, K. 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 (1×10^{-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 (1×10^{-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.

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 1.0×10^{-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.

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

Photonics, Optoelectronics, and Light Manipulation

Moderators: Yohannes Abate, Georgia State University, Nikolaus Dietz, Georgia State University

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Low temperature grown (LTG) GaAs, which is typically obtained by molecular beam epitaxy (MBE) at temperatures as low as 200°C, offers very attractiveproperties such as ultra-short carrier lifetime, high electron mobility and high resistivity. It is verydesirable for applications such as ultrafast photoconductive switch, high efficiency solar cells and infrared LEDs. Pioneering work has demonstrated techniques to bond LTG-GaAs to Si/ SiO_2 at temperature as low as room temperature by means of plasma activation and by wafer bonding under vacuum. However, very few techniques have been developed to bond LTG-GaAs layer to Si_3N_4 substrate, mainly because Si_3N_4 is naturally hydrophobic and bonding has been considered unachievable10. The existing Si_3N_4 bonding techniques employ high temperature fusion of Si_3N_4 layers or apply a layer of bonding agent such as SiO_2.

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

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_2P 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_2CH_3, and $CH_2CH_2CH_3$) 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 2×10^{-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].

References

1. S. Kuld,....... I. Chorkendorff and J. Sehested, Angew. Chemie 53 (2014) 1.

2. C. Holse,....., I. Chorkendorff,S. Helveg, J. H. Nielsen, J. Chem. Phys. 119 (2015) 2804-2812.

3. S. Kuld,..... I. Chorkendorff,J. Sehested, SCIENCE 352 (2016) 969-974.

4. F. Studt, ..., I. Chorkendorff, and J. K. Nørskov, Nature Chemistry. 6 (2014) 320.

5. J. Greeley, ... I. Chorkendorff, J. K. Nørskov, Nature Chemistry. 1 (2009) 522.

6. M. Escudero-Escribano, ..., I. Chorkendorff, SCIENCE 352 (2016) 73-76.

7. P. Hernandez-Fernandez, ... I. Chorkendorff, Nature Chemistry 6 (2014) 732-8.

8. A. Velázquez-Palenzuela,.....I. Chorkendorff, J. Catal. 328 (2015) 297-307.

9. D. Chakraborty, ..., I. Chorkendorff, Accepted Angew. Chemie. (2017).

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 $IrO_2(110)$.

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$_x$Cu$_{1-x}$ 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$_x$Cu$_{1-x}$, 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$_x$Cu$_{1-x}$ size and composition spread nanoparticle (SCSNP) libraries. Spatially resolved X-ray photoemission spectroscopy (XPS) was used to map the Cu 2$p_{3/2}$ core level shifts (CLS) with respect to the value for pure Cu across composition space on the bulk Pd$_x$Cu$_{1-x}$ alloy. The result has shown that the Cu 2$p_{3/2}$ 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 2$p_{3/2}$ core level binding energy measured by XPS can be used to distinguish between the ordered B2 phase and disordered FCC phase. The Pd$_x$Cu$_{1-x}$ SCSNP library on a Mo substrate was prepared using a rotatable shadow mask deposition tool previously developed by our group. After annealing the Pd$_x$Cu$_{1-x}$ 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 2$p_{3/2}$ 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$_x$Cu$_{1-x}$ 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$_x$Cu$_{1-x}$ 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$_x$Cu$_{1-x}$ alloy NPs will be correlated with their catalytic activity across composition and size spaces to accelerate the development of alloy NPs for catalytic applications.

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

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

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

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

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

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

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

9:40am **NS+AS+EM+MI+SP+SS-ThM6 Tunable Emission from Nanophotonic Structures in a Modified SEM: Characterizing Smith Purcell Radiation Generation from the VUV to the Near IR**, ***Steven Kooi***, *I. Kaminer, A. Massuda, M. Soljačić, C. Roques-Carmes*, MIT

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

11:00am **NS+AS+EM+MI+SP+SS-ThM10 Ultrafast Optical Response of Graphene/LaAlO$_3$/SrTiO$_3$ Heterostructure**, *L. Chen, E. Sutton, J. Li, M. Huang, J.F. Hsu, B. D'Urso*, University of Pittsburgh, *J.W. Lee, H. Lee, C.B. Eom*, University of Wisconsin-Madison, *P. Irvin*, ***Jeremy Levy***, University of Pittsburgh **INVITED**

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

We gratefully acknowledge financial support from the following agencies and grants: AFOSR FA9550-12-1-0268 (JL, PRI), AFOSR FA9550-12-1-0342 (CBE)), ONR N00014-13-1-0806 (JL, CBE), NSF DMR-1234096 (CBE), ONR N00014-15-1-2847 (JL) and N00014-16-3152 (JL).

1.Y. Ma, M. Huang, S. Ryu, C. W. Bark, C.-B. Eom, P. Irvin and J. Levy, *NanoLett.***13**, 2884−2888 (2013).

2.G. Jnawali, M. Huang, J.-F. Hsu, H. Lee, J.-W. Lee, P. Irvin, C.-B. Eom, B. D'Urso and J. Levy, *Adv. Mater.* **29**, 1603488 (2016).

3.M. Huang, G. Jnawali, J.-F. Hsu, S. Dhingra, H. Lee, S. Ryu, F. Bi, F. Ghahari, J. Ravichandran, L. Chen, P. Kim, C.-B. Eom, B. D'Urso, P. Irvin and J. Levy, *APL Materials***3**, 062502 (2015).

4.C. Cen, S. Thiel, G. Hammerl, C.W. Schneider, K.E. Andersen, C.S. Hellberg, J. Mannhart, J. Levy, *Nature Materials* **7**, 298 (2008).

5.G. Jnawali, L. Chen, M. Huang, H. Lee, S. Ryu, J. P. Podkaminer, C. B. Eom, P. Irvin and J. Levy, *APL* **106**, 211101 (2015).

11:40am **NS+AS+EM+MI+SP+SS-ThM12 Single-Molecules Fluorescence Spectroscopy and Lifetime with Simultaneous Super-resolution Imaging for Materials Science Applications**, ***James Marr***, CNST/NIST and University of Maryland, *M. Davanço*, CNST/NIST, *S.J. Stranick*, NIST, *B.R. Ilic, J.A. Liddle*, CNST/NIST

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

12:00pm **NS+AS+EM+MI+SP+SS-ThM13 Atomic Scale Surface Effects of Controlled Crystal Structure in III-V Semiconductor Nanowires: Preferential Surface Alloying and Local Electronic Properties.**, *J. Knutsson, M. Hjort*, Lund University, Sweden, *P. Kratzer*, University Duisburg-Essen, Germany, *J. Webb, S. Lehmann, K.D. Thelander*, Lund University, Sweden, *C.J. Palmstrom*, UCSB, *R. Timm*, ***Anders Mikkelsen***, Lund University, Sweden

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

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

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

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

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

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

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

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

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

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

---

* **Coburn & Winters Student Award Finalist**

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.

[1] H.F. Winters, J.W. Coburn, E. Kay, J. Appl. Phys. 48, 4973 (1977)

[2] K.J. Kanarik et al., J. Vac. Sci. Technol. A 33(2) (2015)

[3] K.J. Kanarik et al., J. Vac. Sci. Technol. A 35(5) (2017)

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.

[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).

[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 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

[1] W. Mizubayashi et al., APEX 10, 026501 (2017).

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.

[1] Y. Lee et al., ECS J. Solid State Sci. Technol. 4. N5013 (2015).

[2] K. Shinoda et al., Appl. Phys. Express 9, 106201 (2016).

[3] K. Shinoda et al., J. Phys. D: Appl. Phys. 50, 194001 (2017).

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 4.39×10^{-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.

References

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

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

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

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

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

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

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

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

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

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

The interaction of water with metal oxide surfaces is of great importance in many diverse areas such as catalysis, electrochemistry, corrosion, atmospheric science, geology, astrophysics, and others. Anatase TiO_2 surface is particularly relevant because it is the most active polymorph of TiO_2 and its commercially employed nanomaterials grow preferentially as anatase. In this study, we employ scanning tunneling microscopy (STM) to study the adsorption of water on a model stoichiometric anatase TiO_2(101) surface. Well-defined anatase TiO_2(101) surface has saw-tooth-like morphology exposing alternating rows of two-fold-coordinated oxygen atoms (O_{2c}) and five-fold-coordinated Ti atoms (Ti_{5c}) along the [010] direction. Our STM data show that at 80 K isolated water monomers bind molecularly to the Ti_{5c} sites. The onset of diffusion is found at ~190 K where water monomers diffuse both along and across the Ti_{5c} rows. The analysis shows that the along-the-row diffusion is energetically favored by only 0.03 eV. Surprisingly, we find that at 80 K water molecules start to form linear chains along the Ti_{5c} rows as the coverage is increased. This indicates the presence of transient mobility of water molecules suggesting that the adsorption occurs via a precursor state. When the water chains are annealed at 190 K, they fall apart to monomers that reside on the next-nearest-neighbor Ti_{5c} sites. These results demonstrate that the water chains are metastable in nature. This is at odds with many other oxide surfaces where hydrogen-bonded water clusters are energetically preferred over the isolated monomers.

11:00am **SS+EM+HC+MI-ThM10 The Structure of Fe_2O_3(012) and its Reactivity to Water**, ***Gareth Parkinson****, F. Kraushofer, Z. Jakub, M. Bichler, J. Hulva, M. Schmid, U. Diebold, P. Blaha,* TU Wien, Austria

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

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

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

References

[1] Parkinson, G. S. *Surface Science Reports* **71**, 272-365 (2016).

[2] Henderson, M. A., Joyce, S. A. & Rustad, J. R. *Surface Science* **417**, 66-81 (1998).

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

[4] Gautier-Soyer, M., Pollak, M., Henriot, M. & Guittet, M. *Surface science* **352**, 112-116 (1996).

11:20am **SS+EM+HC+MI-ThM11 Interaction of Water with anatase TiO_2(001)-1x4**, ***Igor Beinik***, *K.C. Adamsen, S. Koust, J.V. Lauritsen, S. Wendt*, Aarhus University, Denmark

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

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

References:

1. Lazzeri, M. & Selloni, A. Phys. Rev. Lett. **87**, 266105 (2001).

2. Yuan, W. et al. Nano Letters **16**, 132–137 (2016).

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

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.

References

1. E. Sutter et al., Nano Letters 16, 21 (2016).
2. T. Björkman et al., ACS Nano 10, 10929 (2016).
3. M. Ghorbani-Asl et al., 2D Materials 4 (2017) 025078.
4. H.-P. Komsa and A.V. Krasheninnikov, Adv. El. Mat. (2017) 1600468.
5. L. Nguyen, et al., ACS Nano 11 (2017) 2894.
6. C. Herbig, et al. Nano Letters (2017) DOI: 10.1021/acs.nanolett.7b00550.
7. S. Kretschmer et al., submitted.

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.

[1] Vashist SK, Luong JH (2015) *Carbon* **84** 519-550.

[2] Suk JW, Kitt A, Magnuson CW *et al.* (2011) *ACS Nano* **5**(9):6916-6924.

[3] Afonso Ferreira J, Stafford L, Leonelli R, Ricard A (2014) *Journal of Applied Physics* **115**(16) 163303.

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.

[1] C. E. Ekuma, V. Dobrosavljevi´c, and D. Gunlycke, Phys. Rev. Lett. 118, 106404 (2017)

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_α (5414.9 eV) and Al K_α (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_α). 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.

[1] Kobayashi, K. Hard X-ray photoemission spectroscopy, *Nucl. Instr. Meth. Phys. Res. A* **2009**, 601, 32-47.

[2] Fadley, C.S. Hard X-ray Photoemission: An Overview and Future Perspective. In Hard X-ray Photoelectron Spectroscopy (HAXPS); Woicik, J. C., Ed; Springer: Switzerland 2016.

[3] Inoue, R., Yamazui, H., Watanabe, K., Newman, J., Mann, J. E., Design and Application of a New Laboratory HAXPES Instrument, ECASIA 2017.

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.

References

S. Bengió, et al. Surf. Sci. 646, 126 - 131 (2016)

B. Eren et al. Science 29, 475-478 (2016)

Z. Duan et al. J. of Solid St. Electrochem. 19, 2265 - 2273 (2015)

K. Samson et al. ACS Catalysis, 4, 373 - 374 (2014)

Yi-Chun Lu et al. Sci. Rep. 2, 715 (2012)

C. S. Gopinath et al. ChemCatChem 7, 588 – 594 (2015)

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.

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 ≈ 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.

[1] G. Kerherve, D.J. Payne et al., Rev. Sci. Instrum., **88** 033102 (2017)

[2] T. Koitaya at al. Topics in Catalysis, **59** 526 (2016)

[3] B. Eren et al. J. Am. Chem. Soc., **138**, 8207 (2016)

[4] X. Deng et al., Langmuir, **24**, 9474 (2008)

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.

[1] Stüve, E. M. *Chem. Phys. Lett.* **2012,** *519*, 1.

[2] Kreuzer, H. J. *Surf. Sci. Anal.* **2004,** *36*, 372.

[3] Che, F. et al., *Catal. Sci. Technol.* **2014,** 4020.

[4] Che, F. et al., *Phys. Chem. Chem. Phys.* **2014,** *16*, 2399.

[5] Che, F. et al., *J. Catal.* **2015,** *332*, 187.

[6] Che, F. et al., *Appl. Catal. B* **2016,** *195*, 77.

[7] Che, F. et al., *ACS Catal.* **2017,** *7*, 551.

[8] Che, F. et al., *ACS Catal.* **2017,** *under review*.

[9] Che, F. et al., *Angew. Chem. Int. Ed.* **2017,** *129*, 3611.

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.

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).

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 γ^{T} into molecular interactions γ^{LW}, and interactions with electrons donors γ^{+} and acceptors γ^{-}. 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 γ^+ and the other with high γ^- 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 γ^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 γ^T, so that total surface interaction γ^T is not mostly controlled by molecular interactions γ^{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 δ-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.

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

Nanostructures including Heterostructures and Patterning of 2D Materials
Moderators: Huamin Li, University of Buffalo, SUNY, Arkady Krasheninnikov, Helmholtz Zentrum Dresden-Rossendorf, Germany

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

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

References:

1. F. Xia et al. “Two-dimensional material nanophotonics” Nat. Phot. 8, 899 (2016).
2. D. Kozawa *et al.* "Efficient interlayer energy transfer via 2D dipole coupling in $MoSe_2/WS_2$ heterostructures" Nano Lett. 16, 4087 (2016).
3. W. Zhao *et. al.* “Exciton-plasmon coupling and electromagnetically induced transparency in monolayer semiconductors hybridized with Ag nanoparticles” *Adv. Mater.* 28, 2709 (2016).

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

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

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

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

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

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

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

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

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

*** NSTD Postdoc Finalist**

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

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

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

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

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

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

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

References:

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

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

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

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

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

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.

---

* **National Student Award Finalist**

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 $\geq$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 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

---

* **National Student Award Finalist**

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°.

Authors Index

Bold page numbers indicate the presenter

— A —

Aarts, I.G.M.: PS+SS-TuA10, 29
Aballe, L.: SA+AS+HC+SS-WeA9, 55
Abate, Y.: SP+SS+TF-WeM4, 45
Abelson, J.R.: SS-TuP11, 35
Abere, M.J.: SE+2D+NS+SS+TF-WeA8, 56
Ablett, J.M.: SA+AS+HC+SS-TuA10, 31
Acik, M.A.: NS+SS+SU-WeM11, **42**
Adams, D.P.: SE+2D+NS+SS+TF-WeA11, 57; SE+2D+NS+SS+TF-WeA8, **56**
Adamsen, K.C.: SS+EM+HC+MI-ThM11, 72
Addamane, S.: EM+MI+NS+SP+SS-ThM11, 63
Addou, R.: EM+SS-TuA12, 25
Afaneh, T.: 2D+EM+SS+TF-WeM6, **37**
Afsari, S.: SP+AS+MI+NS+SS-TuM1, 18
Agarwal, S.: PS+NS+SS+TF-ThM1, 67
Aguirre-Tostado, F.-S.: AS+MI+SS-TuM5, 12
Ahles, C.F.: EM+SS-TuA1, 23
Ahmadi, A.: NS+EM+MI+SS-TuM4, 17
Ahmed, W.: NS+EM+MN+PS+SS-TuA12, **28**
Ahmed, Z.: NS+EM+MN+PS+SS-TuA11, 27
Ahn, T.: SP+AS+MI+NS+SS-TuA1, 31
Ahsan, A.: SP+AS+MI+NS+SS-TuM4, **18**
Aksyuk, V.A.: NS+EM+MN+PS+SS-TuA1, 26; NS+EM+MN+PS+SS-TuA3, **27**; NS+EM+MN+PS+SS-TuA7, 27; NS+SP+SS-ThA8, 78
Alcantar, N.: SS+AS+HC-MoA10, 10
Aleman, A.: SE+2D+NS+SS+TF-WeA4, 56
Alexandrowicz, G.: SS+HC+NS-WeA9, **58**
Altieri, N.: PS+NS+SS+TF-ThM2, **67**
Altman, E.I.: SP+AS+MI+NS+SS-TuA2, 32; SP+AS+NS+SS-MoM3, 1; SS+HC-TuM12, 21
Altman, M.S.: SS+HC+NS-WeA7, 57
Aluru, N.: 2D+MI+NS+SS+TF-FrM9, 82
Amati, M.: SA+AS+HC+SS-TuA3, 30
Aminane, S.: SS+AS+MI-MoM9, 4
Amino, S.: MI+2D+AC+SA+SS-TuM5, 14
Ammann, M.: AS+BI+SA+SS-ThM12, 62
An, S.: NS+EM+MN+PS+SS-TuA3, 27; NS+SP+SS-ThA8, 78
Anders, A.: SE+PS+SS-ThM4, 69
Anderson, V.R.: EM+SS-TuA9, 24
Anthony, R.: PS+NS+SS-WeM5, **44**
Aouadi, S.M.: SE+2D+NS+SS+TF-WeA9, **57**
Aparicio, F.J.: SE+PS+SS-ThM13, 70
Archibald, R.: SP+2D+AS+NS+SS-MoA11, 9
Aresta, G.: SE+PS+SS-ThM6, 70
Argibay, N.: SE+2D+NS+SS+TF-WeA11, **57**; TR+AS+HI+NS+SS-WeA2, 59
Arguelles, E.F.: MI+2D+AC+SA+SS-TuM5, **14**
Arnadottir, L.: HC+SS-TuA1, **25**
Árnadóttir, L.: NS+MN+MS+SS-WeA9, 52; SS+AS+EM-ThA10, 80; SS+HC-FrM7, 85
Arnott, J.: MN+BI+EM+SS+TR-TuM13, 16
Arthur, Z.N.: SA+AS+HC+SS-WeA4, 54
Artiglia, L.: AS+BI+SA+SS-ThM12, 62
Artyushkova, K.: AS+BI+SA+SS-ThM3, **61**; AS+BI+SA+SS-ThM6, 61
Ashtagiri, A.: SS-TuP3, 34
Askari, S.: PS+NS+SS-WeM4, 44
Aspera, S.: MI+2D+AC+SA+SS-TuM5, 14
Asthagiri, A.: HC+SA+SS-ThM12, 65; SS+EM+HC+MI-ThM3, 71
Atanassov, P.: AS+BI+SA+SS-ThM3, 61
Attenkofer, K.: EM+MI+NS+SP+SS-ThM13, 64
Atwater, H.A.: 2D+MI+NS+SS+TF-FrM7, 81
Auerbach, D.J.: HC+SS-ThA1, **76**
Avila-Bront, L.G.: SS+HC-FrM9, **86**
Aydil, E.S.: PS+NS+SS-WeM10, 44
Aydogan Gokturk, P.: AS+BI+SA+SS-ThM4, **61**

— B —

Babore, A.D.: HC+SA+SS-WeA8, 49; SS-TuP18, 36; SS-TuP7, **35**; SS-WeM5, 46
Babuska, T.F.: SE+2D+NS+SS+TF-WeA11, 57; TR+AS+HI+NS+SS-WeA2, 59
Baddorf, A.P.: SP+AS+MI+NS+SS-TuM3, 18
Baeumer, C.: SA+AS+HC+SS-WeA7, **54**
Bagus, P.S.: AS+MI+SS-TuM10, 13
Bai, S.: SS+AS+MI-MoM9, 4
Bailey, C.: 2D+MI+NS+SS+TF-FrM10, 82
Baird, D.: SS+HC-FrM5, 85
Bajdich, M.: HC+NS+SS-WeM1, 40
Baker, M.: AS+BI+MI+NS+SA+SS-WeM2, 38
Balakrishnan, G.: EM+MI+NS+SP+SS-ThM11, 63
Balicas, L.: 2D+MI+NS+SS+TF-FrM4, 81
Balla, I.: NS+EM+MI+SS-TuM10, 17
Baneton, J.: PS+NS+SS-WeM12, **44**
Banis, M.N.: SA+AS+HC+SS-WeA4, 54
Baraldi, A.: 2D+AS+SS-ThA2, 73
Barja, S.: 2D+BI+MN+SS-TuA9, **23**
Barra, A.: MI+2D+AC+SA+SS-TuM13, 15
Barrett, N.: SA+AS+HC+SS-TuA10, 31
Bartelt, N.: SS+AS+MI-MoM3, 2
Bartynski, R.A.: SS-WeM3, **46**
Battu, A.K.: NS+HC+SS-MoA9, 6; SE+2D+NS+SS+TF-WeA7, **56**
Batzill, M.: 2D+AS+SS-ThA11, 74; SS+EM+HC+MI-ThM2, 71; SS-TuP2, 34
Bäumer, M.: SS-TuP6, 34
Becker, C.: SS-WeM10, 47
Beechem, T.E.: SE+2D+NS+SS+TF-WeA8, 56
Beinik, I.: SS+EM+HC+MI-ThM11, **72**
Belianinov, A.: 2D+AS+SS-ThA6, 73; NS+MN+MS+SS-WeA11, 52
Ben Dhiab, I.: SS+HC-FrM3, 85
Beniwal, S.: HC+SS-ThA11, 77
Bent, S.F.: SS+HC-TuM1, 19
Bernal, R.A.: TR+AS+HI+NS+SS-WeA1, 59
Bernard, M.: SA+AS+HC+SS-TuA10, 31
Bernholc, J.: SP+AS+MI+NS+SS-TuM3, 18
Berry, I.L.: PS+NS+SS+TF-ThM3, 68
Berry, R.: 2D+BI+MN+SS-TuA12, 23
Bertram, T.H.: HC+SA+SS-WeA3, 49
Beton, P.H.: 2D+BI+MN+SS-TuA8, 22
Bichler, M.: SS+EM+HC+MI-ThM10, 71
Bignardi, L.: 2D+AS+SS-ThA2, **73**; SS+EM+HC+MI-ThM2, 71
Bijkerk, F.: SS-WeM6, 46
Bischoff, L.: NS+MN+MS+SS-WeA1, 50
Bittencourt, C.: 2D+BI+MN+SS-TuA7, 22
Blades, W.H.: NS+HC+SS-MoA8, **5**
Blaha, P.: SS+EM+HC+MI-ThM10, 71
Blair, R.: HC+SS-TuA9, 26
Blaisdell-Pijuan, P.: NS+HC+SS-MoA10, **6**
Bliem, R.: SS+HC-TuM5, 20
Blobner, F.: SS+AS+MI-MoM8, 3
Blue, B.T.: NS+EM+MI+SS-TuM4, 17; SS-TuP19, **36**
Bluhm, H.: SS+AS+HC-MoA11, 11; SS+HC-TuM11, 21
Boivin, S.: PS+AS+SS-MoA4, 7
Bolotin, K.: SP+SS+TF-WeM4, 45
Bolte, M.: SS+AS+MI-MoM8, 3
Borchers, J.: MI+2D+AC+SA+SS-TuM13, 15
Borguet, E.: SP+AS+MI+NS+SS-TuM1, 18
Boris, D.R.: PS+NS+SS+TF-FrM6, 83
Boulle, O.: SA+AS+HC+SS-WeA9, 55
Boyce, B.L.: SE+2D+NS+SS+TF-WeA11, 57
Boyd, R.: PS+NS+SS-WeM4, 44
Boyko, T.D.: SA+AS+HC+SS-WeA4, 54
Brandt, A.J.: HC+NS+SS-WeM12, 41
Bravo-Sanchez, M.: AS+MI+SS-TuM11, 13
Brenning, N.: PS+NS+SS-WeM4, 44
Bright, V.M.: PS+NS+SS+TF-ThM5, 68
Brimhall, A.: EM+SS-TuA7, 24
Broderick, A.: AS+BI+SA+SS-ThM5, 61
Brooks, A.S.: SE+PS+SS-ThM6, 70
Brown, C.C.: 2D+AS+SS-ThA6, 73; NS+SP+SS-ThA9, 78
Brown, K.A.: NS+MN+MS+SS-WeA4, **51**
Brown-Heft, T.: 2D+EM+SS+TF-WeM5, 37
Bruce, J.P.: HC+SA+SS-WeA8, 49; SS+HC-TuM6, 20; SS-WeM5, **46**
Brumbach, M.T.: AS+BI+MI+NS+SA+SS-WeM12, 39; AS+MI+SS-TuM12, **13**
Brundle, C.R.: AS+MI+SS-TuM10, **13**; AS+MI+SS-TuM6, 13
Buenermann, O.: HC+SS-ThA1, 76
Burch, M.J.: 2D+AS+SS-ThA6, 73; NS+MN+MS+SS-WeA11, 52
Burnham, N.A.: SP+SS+TF-WeM3, **45**
Busby, Y.: PS+NS+SS-WeM12, 44
Busnengo, H.F.: HC+SS-ThA6, **76**

— C —

Cabrera, G.: MI+2D+AC+SA+SS-TuM12, 15
Cabrera-German, D.: AS+MI+SS-TuM11, 13; AS+MI+SS-TuM13, **14**; AS+MI+SS-TuM5, 12
Cahen, D.: NS+SS+SU-WeM3, **42**
Cai, J.: SA+AS+HC+SS-WeA1, 54
Cai, J.M.: HC+SS-ThA9, 77
Cai, L.: SS+AS+HC-MoA8, 10
Caldarella, G.: PS+NS+SS-WeM12, 44
Campbell, C.: HC+SS-ThA10, 77; HC+SS-TuA1, 25
Campbell, P.M.: 2D+BI+MN+SS-TuA2, 22
Campion, R.: SP+2D+AS+NS+SS-MoA3, 8
Cao, K.: SS-TuP20, 36
Cao, Y.: NS+EM+MN+PS+SS-TuA2, 26
Carey, S.: HC+SS-ThA10, 77
Carlson, E.: EM+MI+NS+SP+SS-ThM10, 63
Carman, G.P.: MI+2D+AC+SA+SS-TuM13, 15
Carpick, R.W.: TR+AS+HI+NS+SS-WeA1, 59
Castaneda, V.: SA+AS+HC+SS-TuA12, 31
Castro, G.R.: SA+AS+HC+SS-TuA11, **31**
Centrone, A.: NS+SP+SS-ThA8, 78
Chabal, Y.J.: SS+AS+HC-MoA6, 10
Chae, J.: NS+SP+SS-ThA8, 78
Chan, L.: EM+MI+NS+SP+SS-ThM5, 63
Chandross, M.: SE+2D+NS+SS+TF-WeA11, 57; TR+AS+HI+NS+SS-WeA2, 59
Chang, G.: SP+AS+NS+SS-MoM10, 2
Chang, H.: NS+SP+SS-ThA11, **79**; SP+AS+MI+NS+SS-TuA10, 33
Chang, J.P.: MI+2D+AC+SA+SS-TuM13, 15; PS+NS+SS+TF-ThM2, 67; PS+SS-TuA8, **29**
Chang, S.A.: HC+SA+SS-ThM1, **64**
Chatterjee, S.: AS+SS-ThA6, 75
Chaves, D.S.: SA+AS+HC+SS-WeA9, 55
Che, F.L.: HC+SS-ThA8, **77**
Chen, C.: MN+BI+EM+SS+TR-TuM5, 16
Chen, D.A.: HC+NS+SS-WeM12, **41**
Chen, E.: PS+NS+SS+TF-ThM2, 67
Chen, J.H.: NS+HC+SS-MoA5, 5
Chen, J.K.: PS+NS+SS+TF-ThM2, 67
Chen, J.M.: AS+BI+MI+NS+SA+SS-WeM1, 38
Chen, L.: NS+AS+EM+MI+SP+SS-ThM10, 66
Chen, M.: SS+AS+EM-ThA4, **79**
Chen, P.: TR+AS+HI+NS+SS-WeA1, 59
Chen, P.H.: SS+AS+MI-MoM10, 4
Chen, R.: HC+SS-ThA9, 77; SS-TuP20, 36
Chen, Y.P.: SP+2D+AS+NS+SS-MoA4, 9
Chen, Z.: SS+AS+HC-MoA8, 10
Chiang, S.: SS+HC+NS-WeA7, 57; SS-WeM4, **46**
Chin, Y.Y.: SS+AS+MI-MoM10, 4
Chinone, N.: SP+AS+MI+NS+SS-TuA7, 32
Chirita, V.: SE+2D+NS+SS+TF-WeA12, 57

Cho, K.J.: EM+SS-TuA12, 25
Cho, S.U.: NS+EM+MI+SS-TuM11, 18
Cho, Y.: SP+AS+MI+NS+SS-TuA7, **32**
Choi, J.: EM+SS-TuA1, **23**
Choi, S.: EM+SS-TuA9, 24
Chojnacky, M.J.: NS+EM+MN+PS+SS-TuA11, 27
Chorkendorff, I.: HC+SA+SS-ThM10, **65**
Chow, R.: AS+BI+MI+NS+SA+SS-WeM12, 39
Chu, P.K.: SE+PS+SS-ThM10, **70**
Chuang, T.H.: SS+AS+MI-MoM5, 3
Clark, B.D.: AS+SS-ThA11, 75
Clark, B.G.: SE+2D+NS+SS+TF-WeA11, 57
Clauser, A.L.: SS+HC-FrM7, 85
Cohen, S.R.: MN+BI+EM+SS+TR-TuM12, **16**
Collins, L.: SP+AS+MI+NS+SS-TuA11, 33; SP+AS+MI+NS+SS-TuA12, **33**
Coloma Ribera, R.: SS-WeM6, 46
Cooper, D.: SA+AS+HC+SS-WeA7, 54
Copeland, C.R.: NS+AS+EM+MI+SP+SS-ThM5, 66
Cormier, P.-A.: NS+SS+SU-WeM10, **42**
Cortazar-Martínez, O.: AS+MI+SS-TuM5, 12
Coulter, K.: SE+PS+SS-ThM3, 69
Coy Diaz, H.: 2D+AS+SS-ThA11, **74**
Crist, B.V,: AS+MI+SS-TuM6, **13**
Cristaudo, V.: AS+BI+MI+NS+SA+SS-WeM6, 39
Crommie, M.F.: 2D+BI+MN+SS-TuA9, 23
Cronin, S.: NS+EM+MN+PS+SS-TuA8, 27
Culbertson, J.C.: 2D+BI+MN+SS-TuA2, 22
Culbertson, R.J.: EM+SS-TuA7, 24
Cummings, M.: NS+SP+SS-ThA11, 79
Cumpson, P.J.: AS+SS-ThA8, 75
Currie, M.: 2D+MI+NS+SS+TF-FrM3, 81
Curry, J.F.: SE+2D+NS+SS+TF-WeA11, 57; TR+AS+HI+NS+SS-WeA2, **59**
Curtiss, L.: SP+AS+MI+NS+SS-TuA10, 33; TR+AS+HI+NS+SS-WeA11, 59
Cyganik, P.: SS+AS+MI-MoM8, **3**
Czaplewski, D.A.: MN+BI+EM+SS+TR-TuM5, **16**

— D —

Dagdeviren, O.E.: SP+AS+MI+NS+SS-TuA2, 32; SP+AS+NS+SS-MoM3, **1**
Dahal, A.: SS+EM+HC+MI-ThM6, **71**
Dalmiglio, M.: 2D+AS+SS-ThA2, 73
Daniels, K.M.: 2D+EM+SS+TF-WeM5, 37
Davanço, M.: NS+AS+EM+MI+SP+SS-ThM12, 67
Davis, R.F.: NS+MN+MS+SS-WeA10, 52
Dawson, B.: SS-TuP19, 36
De Alba, R.: NS+EM+MN+PS+SS-TuA1, 26
De la Cruz, W.: AS+MI+SS-TuM13, 14
de Vries, H.W.: PS+SS+TF-WeA3, 53
Debaille, V.: PS+NS+SS-WeM12, 44
Debouge, W.: PS+NS+SS-WeM12, 44
Deeks, C.: AS+BI+MI+NS+SA+SS-WeM2, **38**
del Cueto, M.: SS+HC+NS-WeA12, 58
Delcorte, A.D.: AS+BI+MI+NS+SA+SS-WeM6, **39**
DeMeo, D.: EM+MI+NS+SP+SS-ThM10, 63
Demkov, A.: SS-WeM11, 47
Denbaars, S.: EM+MI+NS+SP+SS-ThM5, 63
Deng, X.: SS+AS+MI-MoM4, **3**; SS+EM+HC+MI-ThM5, 71
Dennis, B.: NS+EM+MN+PS+SS-TuA3, 27
Deprez, S.: SE+PS+SS-ThM13, 70
Dervaux, J.: NS+SS+SU-WeM10, 42
Despiau-Pujo, E.: PS+NS+SS+TF-FrM8, 84
Dew, S.K.: NS+EM+MN+PS+SS-TuA2, 26
Dhesi, S.: SP+2D+AS+NS+SS-MoA3, 8
Di Santo, G.: 2D+BI+MN+SS-TuA7, 22
Diaz, C.: SS+HC+NS-WeA12, 58
Dickerson, J.: AS+MI+SS-TuM12, 13
Dieblod, U.: SS+HC-TuM5, 20
Diebold, A.C.: NS+EM+MI+SS-TuM1, **17**
Diebold, U.: NS+HC+SS-MoA3, **5**; SS+EM+HC+MI-ThM10, 71
Dino, W.A.: MI+2D+AC+SA+SS-TuM5, 14
Dittmann, R.: SA+AS+HC+SS-WeA7, 54
Diulus, J.T.: NS+MN+MS+SS-WeA9, 52
Dohnálek, Z.: SS+EM+HC+MI-ThM6, 71
Dombrowski, E.K.: HC+SS-ThA3, 76; SS+HC+NS-WeA11, 58
Donmez, S.E.: AS+BI+SA+SS-ThM4, 61
Donnelly, V.M.: PS+AS+SS-MoA6, 7; PS+SS-TuA2, **28**
Dorenkamp, Y.: HC+SS-ThA1, 76
DorMohammadi, H.: SS+AS+EM-ThA10, 80
Dorsett, A.L.: SS-WeM4, 46
Douglass, K.O.: NS+EM+MN+PS+SS-TuA11, 27
Dowben, P.A.: HC+SS-ThA11, 77; HC+SS-TuA11, 26
Du, R.: NS+EM+MN+PS+SS-TuA2, 26
Du, Y.: NS+HC+SS-MoA2, **5**
Dugger, M.T.: SE+2D+NS+SS+TF-WeA11, 57
Duncan, A.: NS+SP+SS-ThA4, 78
D'Urso, B.: NS+AS+EM+MI+SP+SS-ThM10, 66
Duscher, G.: 2D+AS+SS-ThA9, 74
Dutoi, A.: AS+MI+SS-TuM5, 12
Dutta, S.: SS+HC-FrM2, **85**
Dynes, J.: SA+AS+HC+SS-WeA4, 54
Dzara, M.J.: AS+BI+SA+SS-ThM3, 61; AS+BI+SA+SS-ThM6, **61**

— E —

Ebnonnasir, A.: SE+2D+NS+SS+TF-WeA4, 56
Economou, D.J.: PS+AS+SS-MoA6, 7
Eda, G.: 2D+MI+NS+SS+TF-FrM1, **81**
Eddy, Jr., C.R.: 2D+EM+SS+TF-WeM5, 37; EM+SS-TuA9, 24
Edinger, K.: PS+AS+SS-MoA8, 7
Edmonds, K.: SP+2D+AS+NS+SS-MoA3, 8
Edmonds, M.T.: SP+AS+NS+SS-MoM10, 2
Edström, D.: SE+2D+NS+SS+TF-WeA12, **57**
Egberts, P.: TR+AS+HI+NS+SS-WeA3, **59**
Eichhorn, B.: SS+HC-TuM11, 21
Eichmann, S.L.: SP+SS+TF-WeM3, 45
Eisele, M.: SP+AS+MI+NS+SS-TuA9, **32**
Ekerdt, J.G.: SS-WeM11, 47
Ekeroth, S.: PS+NS+SS-WeM4, 44
Ekuma, C.: 2D+AS+SS-ThA8, **73**
Elam, F.M.: PS+SS+TF-WeA3, **53**
Endo, K.: PS+NS+SS+TF-FrM9, 84; PS+NS+SS+TF-ThM10, **68**
Engelhard, M.H.: AS+SS-ThA6, 75
Engelmann, H.-J.: NS+MN+MS+SS-WeA1, 50
Engelmann, S.U.: PS+NS+SS+TF-FrM6, 83; PS+SS-TuA3, **28**
Engeln, R.: PS+AS+SS-MoA10, 8
Eom, C.B.: NS+AS+EM+MI+SP+SS-ThM10, 66
Eom, D.: SS+AS+EM-ThA8, **80**
Evans, P.: HC+SS-ThA11, **77**
Evoy, S.: NS+EM+MN+PS+SS-TuA2, **26**

— F —

Facsko, S.: NS+MN+MS+SS-WeA1, 50
Fali, A.: SP+SS+TF-WeM4, 45
Fan, Q.T.: SS+HC-TuM2, 19
Fankhauser, J.: SE+2D+NS+SS+TF-WeA4, 56
Farber, R.G.: HC+SA+SS-WeA10, **50**
Farmakidis, N.: NS+MN+MS+SS-WeA4, 51
Fatayer, S.: SP+AS+MI+NS+SS-TuM4, 18
Faupel, F.: SA+AS+HC+SS-WeA12, 55
Fears, K.P.: SS+HC-TuM11, 21
Feng, X.: HC+NS+SS-WeM4, **41**
Fenner, M.: SP+AS+NS+SS-MoM4, 1
Ferrah, D.: HC+SA+SS-WeA8, **49**; SS+HC-TuM6, 20
Fester, J.: HC+NS+SS-WeM1, **40**; SS+EM+HC+MI-ThM1, 71
Feulner, P.: SS+AS+MI-MoM8, 3
Filler, M.A.: EM+MI+NS+SP+SS-ThM6, **63**
Fisher, B.: TR+AS+HI+NS+SS-WeA11, 59
Fisher, E.R.: NS+HC+SS-MoA6, 5; PS+AS+SS-MoA1, 6; PS+NS+SS-WeM11, 44; PS+SS-TuA12, **29**
Fisher, M.: NS+SP+SS-ThA3, 78
Flaherty, D.W.: HC+SA+SS-ThM1, 64
Fockaert, L.-L.: SS+AS+HC-MoA11, 11
Foerster, M.U.J.: SA+AS+HC+SS-WeA9, 55
Fong, K.: HC+NS+SS-WeM2, 40
Forrest, E.: SS-WeM13, 48
Fourkas, J.T.: PS+AS+SS-MoA5, 7
Franchini, C.: SS+HC-TuM5, 20
Francis, L.: PS+NS+SS-WeM10, 44
Frankcombe, T.: SS+HC+NS-WeA12, 58
Franz, R.: SE+PS+SS-ThM4, 69
Frederick, R.T.: NS+MN+MS+SS-WeA9, 52
Freeland, J.W.: NS+SP+SS-ThA11, 79
Friedman, A.L.: 2D+BI+MN+SS-TuA2, **22**
Froemel, J.: MN+BI+EM+SS+TR-TuM6, 16
Fu, X.: EM+MI+NS+SP+SS-ThM13, 64
Fu, Y.: AS+BI+MI+NS+SA+SS-WeM1, **38**
Fuentes, E.: SS+AS+HC-MoA6, 10
Fuhrer, M.: SP+AS+NS+SS-MoM10, 2
Fukasawa, K.: SS-TuP4, 34
Fukasawa, M.: PS+AS+SS-MoA2, 6; PS+AS+SS-MoA9, 8
Fuller, N.C.M.: PS+SS-TuA3, 28
Furnish, T.A.: SE+2D+NS+SS+TF-WeA11, 57
Füser, M.: 2D+EM+SS+TF-WeM10, 38

— G —

Gabris, C.A.: SS-WeM4, 46
Gage, S.: HC+NS+SS-WeM2, **40**
Gai, Z.: SP+2D+AS+NS+SS-MoA10, 9
Galhenage, R.P.: HC+SA+SS-WeA8, 49; SS+HC-TuM6, **20**; SS-WeM5, 46
Gallagher, N.: AS+SS-ThA6, 75
Gamage, S.: SP+SS+TF-WeM4, **45**
Gao, F.: SS+AS+MI-MoM9, 4; SS+HC-FrM3, 85
Gao, T.: SS+AS+EM-ThA7, **80**
Gao, X.: EM+SS-TuA8, 24
Garcia, N.: SA+AS+HC+SS-TuA12, 31
Garcia, R.: NS+SP+SS-ThA1, 77
Garcia-Melchor, M.: HC+NS+SS-WeM1, 40
Garfunkel, E.L.: NS+MN+MS+SS-WeA9, 52
Garley, A.: 2D+BI+MN+SS-TuA12, **23**
Gaskill, D.K.: 2D+EM+SS+TF-WeM5, 37
Gassilloud, R.: SA+AS+HC+SS-TuA10, 31
Gasvoda, R.J.: PS+NS+SS+TF-ThM1, **67**
Gaudin, G.: SA+AS+HC+SS-WeA9, 55
Geist, J.C.: NS+AS+EM+MI+SP+SS-ThM5, 66
Gelb, L.D.: AS+SS-ThA3, **74**
Gellman, A.: HC+NS+SS-WeM10, **41**; NS+AS+EM+MI+SP+SS-ThM2, 66; SS+HC-FrM2, 85
Genma, T.: SS-TuP4, 34
Geohegan, D.B.: 2D+AS+SS-ThA9, 74
George, S.M.: PS+NS+SS+TF-FrM2, 83; PS+NS+SS+TF-FrM7, 84; PS+NS+SS+TF-ThM5, 68
Gertsch, J.C.: PS+NS+SS+TF-ThM5, **68**
Ghafari, A.: 2D+AS+SS-ThA2, 73
Ghahari, F.: MI+2D+AC+SA+SS-TuM2, **14**
Gharbi, A.: NS+MN+MS+SS-WeA1, 50
Girolami, G.S.: SS-TuP11, 35
Glad, X.: 2D+AS+SS-ThA7, **73**; PS+AS+SS-MoA4, 7
Gnatek, D.: SS+AS+MI-MoM8, 3
Godfroid, T.: SE+PS+SS-ThM13, 70
Goetzen, J.: SP+AS+MI+NS+SS-TuA2, 32; SP+AS+NS+SS-MoM3, 1
Gölzhäuser, A.: 2D+EM+SS+TF-WeM10, 38
Gomez-Muñoz, L.: AS+MI+SS-TuM5, 12
Gómez-Sosa, G.: AS+MI+SS-TuM13, 14
Gona, R.S.: 2D+BI+MN+SS-TuA11, **23**
Gong, M.: SS-TuP20, 36
Gong, P.: TR+AS+HI+NS+SS-WeA3, 59
Gong, X.: SS+EM+HC+MI-ThM2, 71
Goodman, J.M.: SS+HC-FrM4, 85
Goodman, K.: HC+SA+SS-WeA11, 50
Goorsky, M.S.: SE+2D+NS+SS+TF-WeA4, 56
Gord, J.R.: HC+SA+SS-WeA3, 49
Gordon, M.J.: EM+MI+NS+SP+SS-ThM5, **63**; PS+NS+SS-WeM12, 44; PS+NS+SS-WeM13, 45
Gorynski, C.: PS+NS+SS-WeM10, 44
Goto, T.: SS-TuP21, 36

Gottscho, R.A.: PS+NS+SS+TF-ThM3, 68
Grant, J.T.: SE+2D+NS+SS+TF-WeA3, 56
Graves, D.B.: PS+SS-TuA7, **29**
Gray, J.: HC+SS-ThA8, 77
Greenberg, B.: PS+NS+SS-WeM10, **44**
Greene, J.: SE+2D+NS+SS+TF-WeA12, 57
Gregoratti, L.: SA+AS+HC+SS-TuA3, 30
Gronbeck, H.: SS-TuP3, 34
Grutter, A.J.: MI+2D+AC+SA+SS-TuM13, 15
Grutter, P.H.: SP+AS+MI+NS+SS-TuA8, 32
Grutzik, S.: NS+EM+MN+PS+SS-TuA1, 26
Guaitella, O.: PS+AS+SS-MoA10, **8**
Guerra, V.: PS+AS+SS-MoA10, 8
Guisinger, N.P.: NS+EM+MI+SS-TuM10, 17
Gunlycke, D.: 2D+AS+SS-ThA8, 73
Guo, F.: SS+AS+HC-MoA10, **10**
Guo, H.X.: SA+AS+HC+SS-WeA3, **54**; SP+AS+NS+SS-MoM9, 2
Gupta, A.: AS+SS-ThA11, 75
Gupta, S.: AS+SS-ThA11, 75
Gutierrez, C.: MI+2D+AC+SA+SS-TuM2, 14
Gutierrez, H.R.: 2D+EM+SS+TF-WeM6, 37; 2D+MI+NS+SS+TF-FrM4, 81
Gutierrez-Razo, S.A.: PS+AS+SS-MoA5, 7

— H —

Ha, S.: HC+SS-ThA8, 77
Hack, J.H.: SS+AS+EM-ThA4, 79
Haehnlein, I.: PS+SS+TF-WeA10, **53**
Hagen, J.: AS+BI+SA+SS-ThM6, 61
Hagmann, J.A.: NS+MN+MS+SS-WeA2, 51; NS+MN+MS+SS-WeA3, 51
Haji-Sheikh, M.: EM+MI+NS+SP+SS-ThM13, 64
Halpegamage, S.: SS+EM+HC+MI-ThM2, **71**
Hamada, I.: HC+SS-TuA3, 25
Hamaguchi, S.: PS+AS+SS-MoA2, 6; PS+NS+SS+TF-ThM12, 69
Hamamoto, Y.: HC+SS-TuA3, 25
Hammouti, S.: PS+SS+TF-WeA2, 52
Han, S.E.: EM+MI+NS+SP+SS-ThM12, 63
Han, S.J.: EM+MI+NS+SP+SS-ThM12, **63**
Han, S.M.: EM+MI+NS+SP+SS-ThM11, 63; EM+MI+NS+SP+SS-ThM12, 63
Han, Y.: SA+AS+HC+SS-WeA1, 54
Hanbicki, A.T.: 2D+BI+MN+SS-TuA2, 22; 2D+MI+NS+SS+TF-FrM3, 81
Hanna, A.R.: PS+AS+SS-MoA1, **6**
Hannagan, R.T.: HC+SA+SS-ThM5, 65
Harb, J.: NS+MN+MS+SS-WeA10, 52
Harrison, J.A.: TR+AS+HI+NS+SS-WeA1, 59
Hasegawa, T.: PS+SS+TF-WeA1, 52
Hasegawa, Y.: SP+2D+AS+NS+SS-MoA8, **9**
Hassanien, A.: SP+AS+MI+NS+SS-TuA10, 33
Haubrichs, R.: 2D+BI+MN+SS-TuA8, 22
Hauffman, T.: SS+AS+HC-MoA11, 11
Havelund, R.: AS+MI+SS-TuM3, **12**
He, C.: SS-TuP5, **34**
Head, A.R.: SS+AS+HC-MoA11, 11; SS+HC-TuM11, 21
Hedlund, J.K.: 2D+EM+SS+TF-WeM1, **37**
Heeren, R.: AS+BI+MI+NS+SA+SS-WeM3, 38
Heinig, K.-H.: NS+MN+MS+SS-WeA1, 50
Heinz, H.: 2D+BI+MN+SS-TuA12, 23
Heligman, D.: NS+EM+MI+SS-TuM4, 17
Hellerstedt, J.: SP+AS+NS+SS-MoM10, 2
Helmersson, U.: PS+NS+SS-WeM4, **44**
Hemminger, J.C.: HC+SA+SS-WeA8, 49; SS+HC-TuM6, 20; SS-TuP18, 36; SS-TuP7, 35; SS-WeM5, 46
Henderson, M.A.: SS+AS+HC-MoA3, 10
Hennighan, G.: SE+PS+SS-ThM6, 70
Henry, M.D.: AS+MI+SS-TuM12, 13
Herbots, N.: EM+SS-TuA7, 24; SS+AS+EM-ThA6, **79**
Herman, G.S.: NS+MN+MS+SS-WeA9, **52**
Herman, T.: NS+EM+MN+PS+SS-TuA11, 27
Hernández, S.C.: PS+NS+SS+TF-FrM6, 83
Herrera-Gomez, A.: AS+MI+SS-TuM11, 13; AS+MI+SS-TuM13, 14; AS+MI+SS-TuM5, **12**
Hersam, M.C.: NS+EM+MI+SS-TuM10, 17; NS+SS+SU-WeM5, **42**
Hershberger, M.T.: SS+HC+NS-WeA7, **57**
Heslop, S.L.: EM+SS-TuA10, **24**
High, E.: HC+SS-ThA3, 76; SS+HC+NS-WeA11, **58**
Hinz, A.: SA+AS+HC+SS-WeA12, 55
Hirata, A.: PS+AS+SS-MoA2, 6
Hite, J.K.: EM+SS-TuA9, 24
Hiyoto, K.: NS+HC+SS-MoA6, **5**
Hjort, M.: NS+AS+EM+MI+SP+SS-ThM13, 67
Hla, S.W.: NS+SP+SS-ThA11, 79; NS+SP+SS-ThA3, 78; SP+AS+MI+NS+SS-TuA10, 33; SS+HC+NS-WeA3, **57**; TR+AS+HI+NS+SS-WeA11, 59
Hlawacek, G.: NS+MN+MS+SS-WeA1, 50
Ho, M.Y.: SS+HC-FrM4, 85
Hodges, D.R.: SA+AS+HC+SS-TuA12, **31**
Hoffman, A.N.: 2D+MI+NS+SS+TF-FrM8, 82
Hofmann, T.: PS+AS+SS-MoA8, 7
Holcomb, M.B.: MI+2D+AC+SA+SS-TuM12, **15**
Holdren, S.: SS+HC-TuM11, 21
Holscher, H.: SP+AS+NS+SS-MoM3, 1
Holybee, B.J.: PS+SS+TF-WeA2, 52
Hone, J.: NS+EM+MI+SS-TuM4, 17
Hong, K.: SP+AS+MI+NS+SS-TuM3, 18
Hori, M.: PS+AS+SS-MoA9, 8
Hosen, M.M.: SP+AS+NS+SS-MoM10, 2
Hoskins, B.: SP+AS+NS+SS-MoM9, 2
Hotz, M.: AS+BI+SA+SS-ThM12, 62
Howard, M.: SP+SS+TF-WeM4, 45
Hsu, J.F.: NS+AS+EM+MI+SP+SS-ThM10, 66
Hsu, Y.J.: SS+AS+MI-MoM10, **4**; SS+AS+MI-MoM5, 3
Hu, S.: SS-WeM11, **47**
Hu, W.: EM+MI+NS+SP+SS-ThM6, 63
Huang, C.-Y.: MI+2D+AC+SA+SS-TuM12, 15
Huang, M.: NS+AS+EM+MI+SP+SS-ThM10, 66
Huang, Q.: HC+SA+SS-ThM3, 64
Huang, S.: PS+SS-TuA11, 29
Huang, Y.L.: SP+AS+MI+NS+SS-TuM12, 19
Huard, C.M.: PS+NS+SS+TF-FrM5, **83**; PS+SS-TuA11, 29
Hubbard, W.: SS-TuP19, 36
Huber, A.: SP+AS+MI+NS+SS-TuA9, 32
Hübner, R.: NS+MN+MS+SS-WeA1, 50
Hudak, B.M.: NS+MN+MS+SS-WeA7, 51
Hudson, E.A.: PS+NS+SS+TF-ThM1, 67
Hughes, T.L.: SS+HC-FrM4, 85
Hultman, L.: SE+2D+NS+SS+TF-WeA12, 57
Hulva, J.: SS+EM+HC+MI-ThM10, 71; SS+HC-TuM5, **20**
Hund, Z.M.: SS+HC+NS-WeA12, 58
Hung, R.: EM+SS-TuA1, 23
Hunt, A.: SS+HC-TuM6, 20
Hupalo, M.: SS+HC+NS-WeA7, 57
Hus, S.M.: SP+2D+AS+NS+SS-MoA4, 9
Hutchings, G.S.: SS+HC-TuM12, 21
Hutchison, D.: NS+MN+MS+SS-WeA9, 52
Hyde, L.D.: PS+SS+TF-WeA11, 53

— I —

Idrobe, J.: 2D+AS+SS-ThA9, 74
Ievlev, A.V.: 2D+AS+SS-ThA6, 73; NS+MN+MS+SS-WeA11, **52**
Ihlefeld, J.: AS+MI+SS-TuM12, 13
Ilic, B.R.: NS+AS+EM+MI+SP+SS-ThM12, 67; NS+AS+EM+MI+SP+SS-ThM5, 66; NS+EM+MN+PS+SS-TuA1, 26
Inagaki, K.: HC+SS-TuA3, 25
Inoue, R.: AS+SS-ThA9, 75
Irvin, P.: NS+AS+EM+MI+SP+SS-ThM10, 66
Isbill, S.: HC+SS-TuA10, **26**
Isgor, O.B.: SS+AS+EM-ThA10, 80
Ishidzuka, S.: AS+BI+SA+SS-ThM11, 62; SA+AS+HC+SS-WeA11, 55
Ishigami, M.: NS+EM+MI+SS-TuM4, **17**; SP+AS+NS+SS-MoM10, 2; SS-TuP19, 36
Ishikawa, K.: PS+AS+SS-MoA9, 8
Ishikawa, Y.: PS+NS+SS+TF-ThM10, 68
Iski, E.V.: SS+AS+MI-MoM1, **2**
Islam, R.: EM+SS-TuA7, 24; SS+AS+EM-ThA6, 79
Isobe, M.: PS+NS+SS+TF-ThM12, 69
Ito, T.: PS+NS+SS+TF-ThM12, 69
Iwai, Y.: SS-TuP8, **35**
Iwashita, S.: PS+SS+TF-WeA1, **52**
Iyer, A.: SS+AS+EM-ThA4, 79
Izawa, M.: PS+NS+SS+TF-ThM13, 69

— J —

Jablonski, A.: AS+MI+SS-TuM1, 12
Jackson, L.E.: SS+AS+MI-MoM1, 2
Jagtiani, A.V.: PS+NS+SS+TF-FrM6, 83
Jakowski, J.: 2D+AS+SS-ThA6, 73
Jakub, Z.: SS+EM+HC+MI-ThM10, 71; SS+HC-TuM5, 20
Jamer, M.E.: MI+2D+AC+SA+SS-TuM13, 15
Jang, Y.: PS+SS+TF-WeA4, 53
Janke, S.M.: HC+SS-ThA1, 76
Jariwala, D.J.: 2D+MI+NS+SS+TF-FrM7, **81**
Jarvis, K.L.: PS+SS+TF-WeA11, **53**
Je, S.G.: SA+AS+HC+SS-WeA9, 55
Jeng, Y.-R.: TR+AS+HI+NS+SS-WeA1, 59
Jenkins, S.J.: SS+HC-FrM4, 85
Jensen, S.: SS+AS+HC-MoA6, 10
Jeong, H.K.: HC+SS-ThA11, 77
Jernigan, G.G.: 2D+BI+MN+SS-TuA2, 22
Jesse, S.: 2D+AS+SS-ThA6, 73; AS+SS-ThA1, 74; NS+MN+MS+SS-WeA11, 52; NS+SP+SS-ThA9, 78; SP+2D+AS+NS+SS-MoA11, 9; SP+AS+MI+NS+SS-TuA11, **33**; SP+AS+MI+NS+SS-TuA12, 33; SP+AS+NS+SS-MoM8, 1
Jhang, J.-H.: SS+HC-TuM12, **21**
Ji, Y.J.: PS+AS+SS-MoA3, **7**; PS+NS+SS+TF-ThM6, 68; SE+PS+SS-ThM5, 70
Jiang, H.: HC+SS-ThA1, 76
Jiang, N.: NS+AS+EM+MI+SP+SS-ThM1, **65**
Jiang, T.: HC+SS-TuA11, 26; HC+SS-TuA9, **26**
Jin, Y.: PS+SS+TF-WeA4, 53
Jo, M.: NS+EM+MI+SS-TuM11, 18
Job, N.: PS+NS+SS-WeM12, 44
Johnson, A.T.: 2D+BI+MN+SS-TuA11, 23
Johnson, N.: PS+NS+SS+TF-FrM2, **83**
Johnson, W.: EM+SS-TuA8, 24
Jones, J.: AS+SS-ThA11, 75
Jonker, B.T.: 2D+MI+NS+SS+TF-FrM3, 81
Joseph, E.A.: PS+NS+SS+TF-FrM6, 83
Joubert, O.: PS+NS+SS+TF-FrM8, 84
Juge, R.: SA+AS+HC+SS-WeA9, 55
Jung, T.A.: SP+AS+MI+NS+SS-TuM4, 18
Jungwirth, T.: SP+2D+AS+NS+SS-MoA3, 8
Jurczyk, B.E.: PS+SS+TF-WeA10, 53; PS+SS+TF-WeA2, 52

— K —

Kabat, N.W.: SS+AS+MI-MoM11, **4**
Kaczorowski, D.: SP+AS+NS+SS-MoM10, 2
Kaden, W.E.: SS-TuP9, 35
Kahk, J.M.: HC+SS-ThA4, 76
Kaiser, D.: 2D+EM+SS+TF-WeM10, 38
Kaiser, U.: 2D+EM+SS+TF-WeM10, 38
Kalanyan, B.: 2D+EM+SS+TF-WeM2, **37**
Kalinin, S.V.: AS+SS-ThA1, 74; NS+MN+MS+SS-WeA11, 52; SP+2D+AS+NS+SS-MoA11, 9; SP+AS+MI+NS+SS-TuA11, 33; SP+AS+MI+NS+SS-TuA12, 33; SP+AS+NS+SS-MoM8, 1
Kaminer, I.: NS+AS+EM+MI+SP+SS-ThM6, 66
Kanarik, K.: PS+NS+SS+TF-ThM3, 68
Kandratsenka, A.: HC+SS-ThA1, 76
Kaneko, S.: HC+SA+SS-WeA1, 49
Kang, S.: NS+EM+MI+SS-TuM11, 18
Kanjolia, R.: 2D+EM+SS+TF-WeM2, 37
Kao, C.K.: EM+SS-TuA8, 24
Karahashi, K.: PS+AS+SS-MoA2, 6; PS+NS+SS+TF-ThM12, 69
Karslioglu, O.: SS+HC-TuM11, 21

Karslıoğlu, O.: SS+AS+HC-MoA11, 11
Kasai, H.: MI+2D+AC+SA+SS-TuM5, 14
Kasthuri, N.: NS+HC+SS-MoA5, 5
Kaufmann, B.: SS-WeM10, 47
Kavanagh, K.: EM+SS-TuA7, **24**
Kazar Mendes, M.: SA+AS+HC+SS-TuA10, **31**
Keil, S.: SS-TuP6, 34
Keimel, C.: MN+BI+EM+SS+TR-TuM1, **15**
Kerherve, G.: HC+SS-ThA4, 76
Kersell, H.: NS+SP+SS-ThA11, 79
Kessels, W.M.M.: PS+SS-TuA10, 29; PS+SS-TuA4, **28**
Khadka, S.: TR+AS+HI+NS+SS-WeA11, 59
Khalid, M.U.: NS+EM+MN+PS+SS-TuA12, 28
Khalifa, Y.: AS+BI+SA+SS-ThM5, 61
Khan, H.I.: NS+EM+MN+PS+SS-TuA12, 28
Khan, S.: SP+AS+MI+NS+SS-TuA10, 33
Khaniya, A.: SS-TuP9, **35**
Kidwell, D.: 2D+BI+MN+SS-TuA1, 22
Kikuchi, A.: PS+NS+SS+TF-ThM10, 68
Kikuchi, T.: PS+SS+TF-WeA1, 52
Killelea, D.R.: HC+SA+SS-WeA10, 50
Kim, G.-H.: PS+SS+TF-WeA4, 53
Kim, H.J.: PS+SS+TF-WeA7, **53**
Kim, H.K.: SP+AS+MI+NS+SS-TuA1, 31
Kim, K.H.: PS+AS+SS-MoA3, 7; PS+NS+SS+TF-ThM6, 68; SE+PS+SS-ThM5, **70**
Kim, K.S.: PS+AS+SS-MoA3, 7; PS+NS+SS+TF-ThM6, **68**; SE+PS+SS-ThM5, 70
Kim, M.: EM+SS-TuA12, 25; HC+SA+SS-ThM12, 65; SS+EM+HC+MI-ThM3, 71
Kim, N.: EM+SS-TuA1, 23
Kim, N.-K.: PS+SS+TF-WeA4, 53
Kim, P.K.: SS-WeM3, 46
Kim, S.: 2D+AS+SS-ThA6, **73**; NS+MN+MS+SS-WeA11, 52; SS-TuP1, 34
Kim, T.-H.: SP+AS+MI+NS+SS-TuA1, **31**
Kim, Y.: SP+SS+TF-WeM10, **45**
Kimes, W.A.: 2D+EM+SS+TF-WeM2, 37
Kimmel, G.A.: SS+AS+HC-MoA3, **10**
Kind, M.: SS+AS+MI-MoM8, 3
Kirby, B.J.: MI+2D+AC+SA+SS-TuM13, 15
Kishi, Y.: SS-TuP21, 36
Kittell, D.E.: SE+2D+NS+SS+TF-WeA8, 56
Klarenaar, B.: PS+AS+SS-MoA10, 8
Kleyn, A.W.: HC+SA+SS-ThM3, **64**
Klimov, N.N.: NS+EM+MN+PS+SS-TuA11, **27**
Knutsson, J.: NS+AS+EM+MI+SP+SS-ThM13, 67
Ko, W.: SP+2D+AS+NS+SS-MoA4, **9**
Kobashi, M.: SE+2D+NS+SS+TF-WeA4, 56
Kodambaka, S.: SE+2D+NS+SS+TF-WeA4, **56**
Koeble, J.: SP+AS+NS+SS-MoM4, 1
Koel, B.E.: SS+AS+HC-MoA8, **10**
Kollmer, F.: AS+BI+MI+NS+SA+SS-WeM10, **39**
Kolmakov, A.: SA+AS+HC+SS-WeA3, 54; SP+AS+NS+SS-MoM9, 2
Kolmer, M.: SP+AS+NS+SS-MoM5, **1**
Kondo, T.: SS+HC+NS-WeA8, 58; SS+HC-TuM10, 20
Kondratyuk, P.: HC+NS+SS-WeM10, 41
Koo, J.-Y.: SS+AS+EM-ThA8, 80
Kooi, S.E.: NS+AS+EM+MI+SP+SS-ThM6, **66**
Korinko, P.: NS+SP+SS-ThA4, 78
Korolkov, V.V.: 2D+BI+MN+SS-TuA8, **22**
Körstgens, V.: SA+AS+HC+SS-WeA12, 55
Kortshagen, U.R.: PS+NS+SS-WeM10, 44
Koust, S.: SS+EM+HC+MI-ThM11, 72
Kouzuma, Y.: PS+NS+SS+TF-ThM13, 69
Kozarashi, T.: SS+HC+NS-WeA8, 58
Kozen, A.C.: EM+SS-TuA9, 24
Kramer, A.: SS+EM+HC+MI-ThM2, 71
Krasheninnikov, A.V.: 2D+AS+SS-ThA1, **73**
Kratzer, M.: SS-WeM10, 47
Kratzer, P.: NS+AS+EM+MI+SP+SS-ThM13, 67
Kraushofer, F.: SS+EM+HC+MI-ThM10, 71
Krayev, A.: 2D+MI+NS+SS+TF-FrM10, 82; 2D+MI+NS+SS+TF-FrM7, 81
Krick, B.A.: TR+AS+HI+NS+SS-WeA2, 59
Kruppe, C.M.: HC+SA+SS-ThM2, **64**; SS+HC-TuM3, 20
Krylov, S.: NS+EM+MN+PS+SS-TuA1, 26
Kuklja, M.M.: SS+HC-TuM11, 21
Kumari, S.: MI+2D+AC+SA+SS-TuM12, 15
Kummel, A.C.: EM+SS-TuA1, 23
Kushner, M.J.: PS+NS+SS+TF-FrM5, 83; PS+SS-TuA11, **29**
Kustas, A.B.: SE+2D+NS+SS+TF-WeA11, 57

— L —

LaBella, V.: SS+AS+EM-ThA1, **79**
Laboutin, O.: EM+SS-TuA8, 24
Labuda, A.: NS+SP+SS-ThA9, 78
Lacovig, P.: 2D+AS+SS-ThA2, 73; SS+EM+HC+MI-ThM2, 71
Lai, Y.L.: SS+AS+MI-MoM10, 4
Lam, T.N.: SS+AS+MI-MoM10, 4
Lamb, R.N.: MN+BI+EM+SS+TR-TuM13, 16
Landahl, E.: EM+MI+NS+SP+SS-ThM13, 64
Landeros, E.: EM+SS-TuA7, 24
Lang, Y.: SS-TuP20, **36**
Langford, J.M.: SS-TuP18, **36**; SS-TuP7, 35
Lanham, S.J.: PS+SS-TuA11, 29
Larciprete, R.: 2D+AS+SS-ThA2, 73
Larson, A.: SS+HC-FrM10, 86
Larson, A.M.: HC+SA+SS-ThM5, **65**
Latt, K.Z.: SP+AS+MI+NS+SS-TuA10, **33**
Lauritsen, J.V.: HC+NS+SS-WeM1, 40; SS+EM+HC+MI-ThM1, 71; SS+EM+HC+MI-ThM11, 72
Law, K.: SP+2D+AS+NS+SS-MoA11, 9
Le, D.: HC+SS-ThA11, 77; HC+SS-TuA11, 26; HC+SS-TuA9, 26
LeBlanc, G.: SS+AS+MI-MoM1, 2
LeClair, P.R.: AS+SS-ThA11, 75
Lee, C.: SS-TuP6, **34**
Lee, D.: SS-TuP1, 34
Lee, D.G.: SP+AS+MI+NS+SS-TuA1, 31
Lee, G.: NS+SS+SU-WeM11, 42
Lee, H.: NS+AS+EM+MI+SP+SS-ThM10, 66
Lee, J.: SS+AS+MI-MoM4, 3; SS+EM+HC+MI-ThM5, **71**
Lee, J.-H.: NS+EM+MI+SS-TuM11, 18
Lee, J.W.: NS+AS+EM+MI+SP+SS-ThM10, 66
Lee, W.-K.: 2D+BI+MN+SS-TuA1, 22
Lee, Y.: PS+NS+SS+TF-FrM7, **84**
Lehmann, S.: NS+AS+EM+MI+SP+SS-ThM13, 67
Lemaire, P.C.: PS+NS+SS+TF-FrM10, 84
Léoni, T.: SS-WeM10, 47
Leuenberger, D.: AS+BI+SA+SS-ThM12, 62
Levesque, P.: 2D+AS+SS-ThA7, 73
Levitov, L.S.: MI+2D+AC+SA+SS-TuM2, 14
Levy, J.: NS+AS+EM+MI+SP+SS-ThM10, **66**
Lewis, N.S.: SS+HC+NS-WeA12, 58
Ley, R.: EM+MI+NS+SP+SS-ThM5, 63
Li, A.-P.: SP+2D+AS+NS+SS-MoA3, 8; SP+2D+AS+NS+SS-MoA4, 9; SP+AS+MI+NS+SS-TuM3, 18
Li, C.: PS+AS+SS-MoA8, **7**; SE+2D+NS+SS+TF-WeA4, 56
Li, H.: PS+AS+SS-MoA2, **6**; PS+NS+SS+TF-ThM12, 69
Li, J.: NS+AS+EM+MI+SP+SS-ThM10, 66; SS+AS+HC-MoA6, 10
Li, K.: NS+MN+MS+SS-WeA3, 51
Li, L.: SP+2D+AS+NS+SS-MoA10, 9
Li, M.: NS+MN+MS+SS-WeA9, 52
Li, T.: HC+SA+SS-ThM12, **65**; SS+EM+HC+MI-ThM3, 71
Li, X.: 2D+AS+SS-ThA9, 74
Li, Y.: PS+NS+SS+TF-ThM10, 68; SA+AS+HC+SS-WeA1, 54; TR+AS+HI+NS+SS-WeA11, 59
Liang, L.: 2D+AS+SS-ThA9, 74
Liang, Z.: HC+SA+SS-ThM12, 65; SS+EM+HC+MI-ThM3, 71
Libuda, J.: SS+AS+MI-MoM6, **3**
Liddle, J.A.: NS+AS+EM+MI+SP+SS-ThM12, 67; NS+AS+EM+MI+SP+SS-ThM5, 66
Lieber, CM.: TR+AS+HI+NS+SS-WeA9, 59
Lill, T.B.: PS+NS+SS+TF-ThM3, **68**
Lin, H.: SP+AS+NS+SS-MoM10, 2
Lin, H.J.: SS+AS+MI-MoM10, 4
Lin, J.: SE+PS+SS-ThM3, **69**
Lin, M.W.: SS+AS+MI-MoM10, 4
Lin, M.-W.: 2D+AS+SS-ThA9, 74
Linford, M.R.: AS+SS-ThA6, **75**
Lischner, J.: HC+SS-ThA4, 76
List, T.: PS+AS+SS-MoA6, **7**
Liu, J.: SA+AS+HC+SS-WeA1, 54
Liu, P.: HC+SA+SS-WeA11, 50
Liu, Q.: SA+AS+HC+SS-WeA1, 54
Liu, X.: 2D+MI+NS+SS+TF-FrM9, **82**; HC+SS-ThA9, **77**
Liu, X.L.: NS+EM+MI+SS-TuM10, **17**
Liu, Z.: HC+SA+SS-WeA7, **49**; SA+AS+HC+SS-WeA1, **54**
Liu, Z.-F.: 2D+BI+MN+SS-TuA9, 23
Lizzit, S.: 2D+AS+SS-ThA2, 73; SS+EM+HC+MI-ThM2, 71
Lo, C.F.: EM+SS-TuA8, **24**
Locatelli, A.: SA+AS+HC+SS-WeA9, 55
Lodge, M.S.: SP+AS+NS+SS-MoM10, **2**; SS-TuP19, 36
Logan, J.A.: EM+SS-TuA9, 24
Löhrer, F.C.: SA+AS+HC+SS-WeA12, **55**
Long, J.: SS+HC-TuM11, 21
Lopez, D.: MN+BI+EM+SS+TR-TuM5, 16
Lopez, J.: SA+AS+HC+SS-TuA12, 31
Lorenz, M.: NS+SP+SS-ThA9, **78**
Lu, C.I.: SS+AS+MI-MoM5, 3
Lu, D.: SS-WeM3, 46
Lu, K.T.: SS+AS+MI-MoM5, 3
Lu, P.: SE+2D+NS+SS+TF-WeA11, 57
Lu, W.: SP+AS+MI+NS+SS-TuM3, 18
Lubomirsky, I.: MN+BI+EM+SS+TR-TuM12, 16
Ludwig, K.F.: EM+SS-TuA9, 24
Luftman, H.: TR+AS+HI+NS+SS-WeA2, 59
Luijten, E.: NS+EM+MI+SS-TuM10, 17
Lundgren, E.: SS-TuP3, 34
Lundin, D.: SE+PS+SS-ThM1, **69**
Lupini, A.R.: NS+MN+MS+SS-WeA7, **51**
Lyding, J.W.: 2D+MI+NS+SS+TF-FrM9, 82; SP+SS+TF-WeM1, **45**
Lyubinetsky, I.: NS+MN+MS+SS-WeA9, 52

— M —

M. Ugeda, M.: 2D+BI+MN+SS-TuA9, 23
Ma, C.: SP+AS+MI+NS+SS-TuM3, **18**
Ma, T.: HC+SA+SS-WeA2, **49**; PS+AS+SS-MoA6, 7
Ma, Y.: SS-TuP2, **34**
Maccherozzi, F.: SP+2D+AS+NS+SS-MoA3, 8
Mack, P.: AS+BI+MI+NS+SA+SS-WeM2, 38
Mackie, K.E.: PS+NS+SS-WeM13, **45**
Maddumapatabandi, T.D.: HC+NS+SS-WeM12, 41
Mahjouri-Samani, M.: 2D+AS+SS-ThA9, 74
Maier, M.: SP+AS+NS+SS-MoM4, **1**
Majumdar, A.: EM+MI+NS+SP+SS-ThM3, **62**
Makagon, E.: MN+BI+EM+SS+TR-TuM12, 16
Man, M.K.L.: SS+HC+NS-WeA7, 57
Manandhar, S.: NS+HC+SS-MoA9, **6**; SE+2D+NS+SS+TF-WeA7, 56
Mankey, G.J.: AS+SS-ThA11, **75**
Mann, J.E.: AS+SS-ThA9, **75**
Mannix, A.J.: NS+EM+MI+SS-TuM10, 17
Mao, M.: SA+AS+HC+SS-WeA1, 54
Mao, Z.: HC+SS-ThA10, 77
Marchand, H.: EM+SS-TuA8, 24
Marinov, D.: PS+AS+SS-MoA10, 8
Marr, J.M.: NS+AS+EM+MI+SP+SS-ThM12, **67**
Martel, R.: 2D+AS+SS-ThA7, 73
Martin, F.: SS+HC+NS-WeA12, 58
Martinez, E.: SA+AS+HC+SS-TuA10, 31
Martinez, M.: SA+AS+HC+SS-TuA12, 31
Martinez-Blanco, J.: SS-WeM12, 47

Martini, A.: SS-TuP19, 36
Martirosyan, V.: PS+NS+SS+TF-FrM8, **84**
Maslar, J.E.: 2D+EM+SS+TF-WeM2, 37
Masson, L.: SS-WeM10, 47
Massuda, A.: NS+AS+EM+MI+SP+SS-ThM6, 66
Matkovic, A.: SS-WeM10, 47
Mattson, E.: SS+AS+HC-MoA6, 10
Mavrikakis, M.: HC+SS-TuA7, **25**
McArthur, S.L.: PS+SS+TF-WeA11, 53
McClelland, J.J.: SP+AS+NS+SS-MoM9, 2
McClure, Z.L.: SS+HC-FrM7, 85
McCoustra, M.R.S.: SS+HC-FrM5, **85**
McCreary, K.M.: 2D+MI+NS+SS+TF-FrM3, **81**
McDermott, M.T.: NS+EM+MN+PS+SS-TuA2, 26
McEwen, J.-S.: HC+SS-ThA8, 77
McFadden, A.P.: 2D+EM+SS+TF-WeM5, 37
McGehee, W.: SP+AS+NS+SS-MoM9, 2
McGray, C.D.: NS+AS+EM+MI+SP+SS-ThM5, 66
McIntyre, P.C.: EM+SS-TuA3, **23**
McKibbin, S.: SA+AS+HC+SS-TuA3, 30
McLain, J.: PS+SS+TF-WeA10, 53
McNamara, J.: NS+SP+SS-ThA4, **78**
Mehar, V.: SS-TuP3, **34**; SS-TuP6, 34
Meier, M.: SS+HC-TuM5, 20
Memaran, S.: 2D+MI+NS+SS+TF-FrM4, 81
Meng, X.: HC+SA+SS-WeA11, 50
Mentes, T.O.: SA+AS+HC+SS-WeA9, 55
Menzel, S.: SA+AS+HC+SS-WeA7, 54
Meshkova, A.S.: PS+SS+TF-WeA3, 53
Michel, E.G.: SS-WeM12, **47**
Michels, T.: NS+EM+MN+PS+SS-TuA3, 27
Mikkelsen, A.: NS+AS+EM+MI+SP+SS-ThM13, **67**; SA+AS+HC+SS-TuA3, 30
Miline, Z.: TR+AS+HI+NS+SS-WeA1, 59
Miller, J.H.: SS-WeM4, 46
Mishra, A.K.: SA+AS+HC+SS-TuA12, 31
Mishuk, E.: MN+BI+EM+SS+TR-TuM12, 16
Miyahara, Y.: SP+AS+MI+NS+SS-TuA8, **32**
Miyazoe, H.: PS+NS+SS+TF-FrM6, 83
Miyoshi, Y.: PS+AS+SS-MoA9, **8**
Mizubayashi, W.: PS+NS+SS+TF-FrM9, 84; PS+NS+SS+TF-ThM10, 68
Mo, S.-K.: 2D+BI+MN+SS-TuA9, 23; 2D+EM+SS+TF-WeM3, **37**
Moghaddam, S.: NS+SS+SU-WeM12, **43**
Mogi, T.: SS+HC+NS-WeA8, 58
Mohammad, M.A.: NS+EM+MN+PS+SS-TuA2, 26
Mohimi, E.: SS-TuP11, 35
Mohn, M.: 2D+EM+SS+TF-WeM10, 38
Mohr, S.: SS+AS+MI-MoM6, 3
Mol, J.M.C.: SS+AS+HC-MoA11, 11
Molar-Velazquez, G.: AS+MI+SS-TuM13, 14
Monazami, E.: SS+AS+MI-MoM11, 4
Morgan, H.R.: SS+AS+MI-MoM1, 2
Morgan, M.: NS+SP+SS-ThA4, 78
Morgan, S.: HC+SS-ThA10, 77
Morikawa, Y.: HC+SS-TuA3, 25
Morillo-Candas, A.S.: PS+AS+SS-MoA10, 8
Moriya, T.: PS+SS+TF-WeA1, 52
Morris, T.: SS-TuP1, 34
Morse, D.: EM+MI+NS+SP+SS-ThM5, 63
Mottaghi, N.: MI+2D+AC+SA+SS-TuM12, 15
Mousavi, S.F.: SP+AS+MI+NS+SS-TuM4, 18
Mowll, T.R.: 2D+EM+SS+TF-WeM11, **38**
Mucciolo, E.R.: NS+EM+MI+SS-TuM4, 17
Mueller, D.N.: SA+AS+HC+SS-WeA3, 54
Müller-Buschbaum, P.: SA+AS+HC+SS-WeA12, 55
Mullet, C.H.: SS+HC+NS-WeA7, 57
Munoz, J.: SA+AS+HC+SS-TuA12, 31
Muraca, A.R.: SS+AS+HC-MoA5, **10**
Muratore, C.: SE+2D+NS+SS+TF-WeA9, 57
Murphy, N.R.: SE+2D+NS+SS+TF-WeA3, 56
Murray, R.: NS+MN+MS+SS-WeA2, 51; NS+MN+MS+SS-WeA3, 51
Muscat, A.J.: EM+SS-TuA10, 24
Muttaqien, F.: HC+SS-TuA3, **25**
Muzas, A.: SS+HC+NS-WeA12, 58
Myers-Ward, R.L.: 2D+EM+SS+TF-WeM5, 37
Myochi, R.: HC+SA+SS-WeA1, 49

— N —

Nagahata, K.: PS+AS+SS-MoA2, 6; PS+AS+SS-MoA9, 8
Naghibolashrafi, N.: AS+SS-ThA11, 75
Nakamura, J.: SS+HC+NS-WeA8, 58; SS+HC-TuM10, 20
Nakanishi, H.: MI+2D+AC+SA+SS-TuM5, 14
Namboodiri, P.: NS+MN+MS+SS-WeA2, 51; NS+MN+MS+SS-WeA3, 51
Narayanan, B.: TR+AS+HI+NS+SS-WeA11, 59
Nathanson, G.: HC+SA+SS-WeA3, **49**
Nation, B.L.: SE+2D+NS+SS+TF-WeA11, 57
Naylor, C.H.: 2D+BI+MN+SS-TuA11, 23
Neaton, J.B.: 2D+BI+MN+SS-TuA9, 23
Nelson, G.: PS+NS+SS-WeM10, 44
Nemšák, S.: SA+AS+HC+SS-WeA3, 54
Nepal, N.: EM+SS-TuA9, 24
Neumann, C.: 2D+EM+SS+TF-WeM10, **38**
Neupane, M.: SP+AS+NS+SS-MoM10, 2
Newberg, J.T.: AS+BI+SA+SS-ThM5, **61**
Newman, J.: AS+SS-ThA9, 75
Ngo, A.: SP+AS+MI+NS+SS-TuA10, 33; TR+AS+HI+NS+SS-WeA11, 59
Ngo, C.: AS+BI+SA+SS-ThM6, 61; HC+NS+SS-WeM2, 40
Nguyen, G.: SP+2D+AS+NS+SS-MoA3, **8**
Nguyen, M.P.: MN+BI+EM+SS+TR-TuM6, **16**
Nihill, K.: SS+HC+NS-WeA12, **58**
Nijs, T.: SP+AS+MI+NS+SS-TuM4, 18
Nishi, T.: PS+NS+SS+TF-ThM10, 68
Noda, S.: PS+NS+SS+TF-FrM9, **84**; PS+NS+SS+TF-ThM10, 68
Nolting, W.: SS+AS+EM-ThA1, 79
Nordlund, D.: AS+MI+SS-TuM5, 12; HC+NS+SS-WeM2, 40
Noro, N.: PS+SS+TF-WeA1, 52
Novotny, Z.N.: AS+BI+SA+SS-ThM12, **62**
Nowakowska, S.: SP+AS+MI+NS+SS-TuM4, 18
Noworolska, A.: SS+AS+MI-MoM8, 3
Noyce, S.: NS+MN+MS+SS-WeA10, 52
Nyman, M.: NS+MN+MS+SS-WeA9, 52

— O —

O'Brien, C.J.: SE+2D+NS+SS+TF-WeA11, 57
Ocola, L.E.: NS+HC+SS-MoA10, 6; NS+HC+SS-MoA5, **5**
Odobel, F.: NS+SS+SU-WeM10, 42
Odom, T.W.: EM+MI+NS+SP+SS-ThM1, **62**
Oehrlein, G.S.: PS+AS+SS-MoA5, 7; PS+AS+SS-MoA8, 7; PS+SS-TuA9, **29**
Ogasawara, H.: NS+MN+MS+SS-WeA9, 52
Ogawa, S.: AS+BI+SA+SS-ThM10, 62; AS+BI+SA+SS-ThM11, 62; SA+AS+HC+SS-WeA11, **55**
Ogletree, D.F.: 2D+BI+MN+SS-TuA9, 23
Ogrinc Potocnik, N.: AS+BI+MI+NS+SA+SS-WeM3, **38**
Oh, J.S.: SE+PS+SS-ThM5, 70
Ohlhausen, J.A.: AS+BI+MI+NS+SA+SS-WeM12, **39**
Okada, Y.: PS+NS+SS+TF-ThM12, **69**
Okura, T.: SS-TuP4, 34; SS-TuP8, 35
Oliva, A.: SS-WeM12, 47
Olsen, M.R.: NS+MN+MS+SS-WeA9, 52
Opila, R.L.: SS+AS+EM-ThA4, 79
Orlando, F.: 2D+AS+SS-ThA2, 73; AS+BI+SA+SS-ThM12, 62
Oshima, H.: HC+SS-TuA3, 25
Ossowski, J.: SS+AS+MI-MoM8, 3
Osterwalder, J.: AS+BI+SA+SS-ThM12, 62
Ostrikov, K.: PS+NS+SS-WeM1, **43**
Ota, H.: PS+NS+SS+TF-ThM10, 68
Ovchinnikova, O.S.: 2D+AS+SS-ThA6, 73; AS+SS-ThA1, 74; NS+MN+MS+SS-WeA11, 52; NS+SP+SS-ThA9, 78
Oware Sarfo, K.: SS+HC-FrM7, **85**
Owrutsky, J.: SS+HC-TuM11, 21
Oyedele, A.: 2D+AS+SS-ThA9, 74

— P —

Palmstrom, C.J.: NS+AS+EM+MI+SP+SS-ThM13, 67
Palmstrøm, C.J.: 2D+EM+SS+TF-WeM5, 37; EM+SS-TuA9, 24
Pan, Y.: PS+NS+SS+TF-ThM3, 68
Pang, Q.: SS+AS+EM-ThA10, **80**
Panjan, M.: SE+PS+SS-ThM4, **69**
Pantelides, S.T.: NS+MN+MS+SS-WeA7, 51
Papa, F.: SE+PS+SS-ThM3, 69
Park, J.: 2D+EM+SS+TF-WeM12, **38**
Park, S.: NS+EM+MI+SS-TuM11, 18; SP+AS+MI+NS+SS-TuM11, **19**
Park, Y.D.: NS+EM+MI+SS-TuM11, **18**
Parker, D.S.: SP+2D+AS+NS+SS-MoA10, 9
Parkinson, G.S.: SS+EM+HC+MI-ThM10, **71**; SS+HC-TuM5, 20
Parsons, G.N.: PS+NS+SS+TF-FrM10, 84
Pasupathy, A.: SP+AS+MI+NS+SS-TuA3, **32**
Patel, D.A.: HC+SA+SS-WeA9, **50**
Paterson, A.: PS+NS+SS+TF-FrM5, 83
Payne, D.J.: HC+SS-ThA4, **76**
Payne, M.A.: HC+NS+SS-WeM10, 41
Peckler, L.: EM+SS-TuA10, 24
Peeters, F.J.J.: PS+SS-TuA10, 29
Pellegrin, Y.: NS+SS+SU-WeM10, 42
Pelzel, R.: EM+SS-TuA8, 24
Pennachio, D.J.: 2D+EM+SS+TF-WeM5, **37**; EM+SS-TuA9, 24
Perego, M.: NS+MN+MS+SS-WeA1, 50
Perkins, F.K.: 2D+BI+MN+SS-TuA2, 22
Perrino, A.: NS+SP+SS-ThA1, 77
Pershad, Y.W.: EM+SS-TuA7, 24
Petaccia, L.: 2D+AS+SS-ThA2, 73; 2D+BI+MN+SS-TuA7, 22
Petrik, N.G.: SS+AS+HC-MoA3, 10
Petrov, I.: SE+2D+NS+SS+TF-WeA12, 57
Pfiester, N.A.: EM+MI+NS+SP+SS-ThM10, **63**
Phillips, J.A.: SS+AS+MI-MoM1, 2
Pianetta, P.: AS+MI+SS-TuM5, 12
Pikma, P.: SP+AS+MI+NS+SS-TuM1, 18
Pipino, A.C.R.: PS+SS-TuA10, 29
Pireaux, J.-J.: PS+NS+SS-WeM12, 44
Pirou, A.: SP+AS+NS+SS-MoM4, 1
Pizzini, S.: SA+AS+HC+SS-WeA9, 55
Plaza, M.: SS-WeM12, 47
Pletincx, S.: SS+AS+HC-MoA11, **11**; SS+HC-TuM11, 21
Plymale, N.: SS+HC+NS-WeA12, 58
Pohl, K.: SS+HC-FrM10, **86**
Poleunis, C.: AS+BI+MI+NS+SA+SS-WeM6, 39
Polonskyi, O.: SA+AS+HC+SS-WeA12, 55
Polop, C.: NS+SP+SS-ThA1, **77**
Pop, E.: 2D+MI+NS+SS+TF-FrM10, 82
Popova, O.: SP+AS+MI+NS+SS-TuM4, 18
Popovitz-Biro, R.: MN+BI+EM+SS+TR-TuM12, 16
Porach, Z.: NS+AS+EM+MI+SP+SS-ThM1, 65
Posadas, A.: SS-WeM11, 47
Pour, M.: 2D+MI+NS+SS+TF-FrM9, 82
Powell, C.J.: AS+MI+SS-TuM1, **12**
Pranda, A.: PS+AS+SS-MoA5, **7**
Proksch, R.: NS+SP+SS-ThA6, **78**; NS+SP+SS-ThA9, 78
Provost, B.: SS+HC-FrM4, **85**
Prüfer, T.: NS+MN+MS+SS-WeA1, 50
Pudasaini, P.R.: 2D+MI+NS+SS+TF-FrM8, 82
Pulkin, A.: 2D+BI+MN+SS-TuA9, 23
Puretzky, A.A.: 2D+AS+SS-ThA9, 74; SP+AS+MI+NS+SS-TuM3, 18
Pylypenko, S.: AS+BI+SA+SS-ThM3, 61; AS+BI+SA+SS-ThM6, 61; HC+NS+SS-WeM2, 40
Pynn, C.: EM+MI+NS+SP+SS-ThM5, 63

— Q —
Qian, X.: 2D+MI+NS+SS+TF-FrM5, **81**
Qiu, D.: 2D+BI+MN+SS-TuA9, 23
Quan, J.M.: SS+HC+NS-WeA8, **58**
Quek, S.Y.: SP+AS+MI+NS+SS-TuM12, 19
Quinn, S.L.: HC+SA+SS-WeA3, 49
Quiros, C.: SS-WeM12, 47
— R —
Rack, P.D.: 2D+MI+NS+SS+TF-FrM8, 82
Radenovic, A.: 2D+BI+MN+SS-TuA3, **22**
Radocea, A.: 2D+MI+NS+SS+TF-FrM9, 82
Rahman, T.S.: HC+SS-ThA11, 77; HC+SS-TuA11, 26; HC+SS-TuA9, 26
Rai, R.: SS+EM+HC+MI-ThM3, 71
Ramalingam, G.: NS+HC+SS-MoA8, 5
Ramana, C.V.: NS+HC+SS-MoA9, 6; SE+2D+NS+SS+TF-WeA7, 56
Ramer, G.: NS+SP+SS-ThA8, **78**
Rand, R.H.: NS+EM+MN+PS+SS-TuA1, 26
Rangan, S.: SS-WeM3, 46
Ranguis, A.: SS-WeM10, 47
Ranjan, A.: PS+NS+SS+TF-FrM1, 82; PS+NS+SS+TF-FrM3, 83
Rawal, T.B.: HC+SS-TuA11, **26**; HC+SS-TuA9, 26
Rechav, K.: MN+BI+EM+SS+TR-TuM12, 16
Refaely-Abramson, S.: 2D+BI+MN+SS-TuA9, 23
Regier, T.Z.: SA+AS+HC+SS-WeA4, **54**
Regoutz, A.: HC+SS-ThA4, 76
Reich, K.: PS+NS+SS-WeM10, 44
Reininger, R.: NS+SP+SS-ThA3, 78
Reinke, P.: NS+HC+SS-MoA8, 5; SS+AS+MI-MoM11, 4
Rementer, C.R.: MI+2D+AC+SA+SS-TuM13, **15**
Renault, O.J.: SA+AS+HC+SS-TuA10, 31
Reniers, F.: PS+NS+SS-WeM12, 44
Reynolds, N.P.: PS+SS+TF-WeA11, 53
Richards, R.: HC+NS+SS-WeM2, 40
Richter, C.: NS+MN+MS+SS-WeA2, 51; NS+MN+MS+SS-WeA3, 51
Rienicker, D.: HC+NS+SS-WeM10, 41
Righi, M.C.: TR+AS+HI+NS+SS-WeA7, **59**
Rimada, M.: EM+MI+NS+SP+SS-ThM11, 63
Robert-Bigras, G.: 2D+AS+SS-ThA7, 73; PS+AS+SS-MoA4, 7
Robinson Brown, D.: AS+MI+SS-TuM12, 13
Robinson, E.: 2D+MI+NS+SS+TF-FrM7, 81
Robinson, J.T.: 2D+BI+MN+SS-TuA1, 22
Robinson, Z.: PS+NS+SS-WeM10, 44
Robinson, Z.R.: 2D+EM+SS+TF-WeM11, 38; EM+SS-TuA9, 24
Rodiguez-Nieva, J.R.: MI+2D+AC+SA+SS-TuM2, 14
Rodriguez, J.: HC+SA+SS-WeA7, 49
Rodriguez, M.A.: SE+2D+NS+SS+TF-WeA11, 57
Rodriguez-Fernandez, J.: SS+EM+HC+MI-ThM1, **71**
Rodríguez-Fernández, J.: HC+NS+SS-WeM1, 40
Rogalev, A.: MI+2D+AC+SA+SS-TuM6, **15**
Roh, H.-J.: PS+SS+TF-WeA4, **53**
Ronda Lloret, M.: HC+SA+SS-ThM3, 64
Roques-Carmes, C.: NS+AS+EM+MI+SP+SS-ThM6, 66
Rose, V.: NS+SP+SS-ThA11, 79; NS+SP+SS-ThA3, **78**
Rosen, J.: SE+2D+NS+SS+TF-WeA1, **56**
Rosenberg, R.A.: NS+SS+SU-WeM11, 42
Rosenberg, S.G.: EM+SS-TuA9, **24**; PS+NS+SS+TF-FrM6, 83
Rosenhahn, A.: MN+BI+EM+SS+TR-TuM13, 16
Rosenmann, D.: NS+SP+SS-ThA11, 79
Ross, S.: EM+MI+NS+SP+SS-ThM13, 64
Rosu-Finsen, A.: SS+HC-FrM5, 85
Roth, S.V.: SA+AS+HC+SS-WeA12, 55
Roth, T.: SP+AS+NS+SS-MoM4, 1
Rothenberg, G.: HC+SA+SS-ThM3, 64
Rouleau, C.M.: 2D+AS+SS-ThA9, 74
Roxworthy, B.J.: NS+EM+MN+PS+SS-TuA3, 27; NS+EM+MN+PS+SS-TuA7, **27**
Roy, S.: HC+SS-TuA10, 26
Roy-Gobeil, A.: SP+AS+MI+NS+SS-TuA8, 32
Rubio Zuazo, J.: SA+AS+HC+SS-TuA11, 31
Ruggieri, C.: SS-WeM3, 46
Rumaiz, A.K.: SA+AS+HC+SS-TuA9, 30
Rummel, B.: EM+MI+NS+SP+SS-ThM11, **63**
Russell, E.M.: SS-WeM4, 46
Ruzic, D.N.: PS+SS+TF-WeA10, 53; PS+SS+TF-WeA2, **52**
Rysz, J.: SS+AS+MI-MoM8, 3
Ryu, H.: 2D+BI+MN+SS-TuA9, 23
Ryu, S.: PS+SS+TF-WeA4, 53
— S —
Sahoo, P.K.: 2D+EM+SS+TF-WeM6, 37; 2D+MI+NS+SS+TF-FrM4, **81**
Saikia, N.: 2D+BI+MN+SS-TuA12, 23
Sakai, S.: PS+NS+SS+TF-ThM13, 69
Salagre, E.: SS-WeM12, 47
Salmeron, M.B.: 2D+BI+MN+SS-TuA9, 23
Saltonstall, C.B.: SE+2D+NS+SS+TF-WeA8, 56
Sampathkumar, V.: NS+HC+SS-MoA5, 5
Samukawa, S.: PS+NS+SS+TF-FrM9, 84; PS+NS+SS+TF-ThM10, 68
Sandoval, T.E.: SS+HC-TuM1, **19**
Sangiovanni, D.: SE+2D+NS+SS+TF-WeA12, 57
Sankaran, R.M.: PS+NS+SS-WeM12, 44; PS+SS-TuA1, **28**
Sankaranarayanan, S.: TR+AS+HI+NS+SS-WeA11, 59
Santala, M.: SS+HC-FrM7, 85
Sato, M.: SE+2D+NS+SS+TF-WeA4, 56
Scardamaglia, M.: 2D+BI+MN+SS-TuA7, **22**
Schall, J.D.: TR+AS+HI+NS+SS-WeA1, **59**
Schelkanov, I.: PS+SS+TF-WeA10, 53
Schmid, M.: SS+EM+HC+MI-ThM10, 71; SS+HC-TuM5, 20
Schmitz, C.: SA+AS+HC+SS-WeA7, 54
Schmucker, S.W.: NS+MN+MS+SS-WeA2, 51; NS+MN+MS+SS-WeA3, 51
Schneider, C.M.: SA+AS+HC+SS-WeA3, 54; SA+AS+HC+SS-WeA7, 54
Schoen, D.: SA+AS+HC+SS-TuA4, **30**
Schröder, M.: 2D+BI+MN+SS-TuA8, 22
Schuler, B.: 2D+BI+MN+SS-TuA9, 23
Schuler, E.: HC+SA+SS-ThM3, 64
Schultz, J.: NS+AS+EM+MI+SP+SS-ThM1, 65
Schuschke, C.: SS+AS+MI-MoM6, 3
Schwartzkopf, M.: SA+AS+HC+SS-WeA12, 55
Schwarz, M.: SS+AS+MI-MoM6, 3
Schwarz, U.D.: SP+AS+MI+NS+SS-TuA2, **32**; SP+AS+NS+SS-MoM3, 1; SS+HC-TuM12, 21
Seal, S.: MN+BI+EM+SS+TR-TuM10, **16**
Sefat, A.: SP+2D+AS+NS+SS-MoA10, 9
Segovia, P.: SS-WeM12, 47
Sekihata, Y.: AS+BI+SA+SS-ThM11, **62**
Sekine, M.: PS+AS+SS-MoA9, 8
Seo, E.: SS+AS+EM-ThA8, 80
Setvin, M.: SS+HC-TuM5, 20
Seuser, G.: HC+NS+SS-WeM12, 41
Sezen, H.: SA+AS+HC+SS-TuA3, 30
Shahriar, S.: SA+AS+HC+SS-TuA12, 31
Shaloski, M.A.: HC+SA+SS-WeA3, 49
Shan, B.: HC+SS-ThA9, 77; SS-TuP20, 36
Shapturenka, P.: EM+MI+NS+SP+SS-ThM5, 63
Shard, A.G.: AS+MI+SS-TuM2, **12**
Sharma, R.: NS+AS+EM+MI+SP+SS-ThM3, **66**
Shaw, S.W.: MN+BI+EM+SS+TR-TuM5, 16
Sheehan, P.E.: 2D+BI+MN+SS-TuA1, 22; TR+AS+HI+NS+SS-WeA9, **59**
Shemelya, C.: EM+MI+NS+SP+SS-ThM10, 63
Shen, Z.-X.: 2D+BI+MN+SS-TuA9, 23
Sherpa, S.D.: PS+NS+SS+TF-FrM1, **82**
Sherrott, M.C.: 2D+MI+NS+SS+TF-FrM7, 81
Shiba, Y.: SS-TuP21, **36**
Shibuya, R.: SS+HC-TuM10, **20**
Shiflett, M.B.: AS+BI+SA+SS-ThM5, 61
Shih, K.: SP+2D+AS+NS+SS-MoA1, **8**
Shiju, N.R.: HC+SA+SS-ThM3, 64
Shinoda, K.: PS+NS+SS+TF-ThM13, 69
Shipilin, M.: SS-TuP3, 34
Shirai, Y.: SS-TuP21, 36
Shirato, N.: NS+SP+SS-ThA11, 79; NS+SP+SS-ThA3, 78
Shirvan, K.: SS-WeM13, **48**
Shklovskii, B.: PS+NS+SS-WeM10, 44
Shulda, S.: HC+NS+SS-WeM2, 40
Sibener, S.J.: SS+HC+NS-WeA12, 58
Silies, L.: SS+AS+MI-MoM8, 3
Silver, R.M.: NS+MN+MS+SS-WeA2, **51**; NS+MN+MS+SS-WeA3, 51
Simmons, M.: NS+EM+MI+SS-TuM5, **17**
Simovich, T.: MN+BI+EM+SS+TR-TuM13, **16**
Sims, H.R.: NS+MN+MS+SS-WeA7, 51
Singh, B.: AS+SS-ThA6, 75; SP+AS+NS+SS-MoM10, 2
Singh, S.V.: SE+PS+SS-ThM6, **70**
Sinitskii, A.: 2D+MI+NS+SS+TF-FrM9, 82
Sinno, T.: EM+MI+NS+SP+SS-ThM11, 63
Siri, O.: SS-WeM10, 47
Slikboer, E.: PS+AS+SS-MoA10, 8
Smith, S.: AS+MI+SS-TuM12, 13
Smithe, K.: 2D+MI+NS+SS+TF-FrM10, **82**
Snijders, P.C.: NS+MN+MS+SS-WeA7, 51
Snyders, R.: 2D+BI+MN+SS-TuA7, 22; NS+SS+SU-WeM10, 42; SE+PS+SS-ThM13, 70
Sobczak, C.: SE+2D+NS+SS+TF-WeA8, 56
Sobota, A.: PS+AS+SS-MoA10, 8
Soljačić, M.: NS+AS+EM+MI+SP+SS-ThM6, 66
Somnath, S.: AS+SS-ThA1, 74; SP+2D+AS+NS+SS-MoA11, 9; SP+AS+NS+SS-MoM8, **1**
Song, B.: NS+EM+MN+PS+SS-TuA8, 27
Song, J.: NS+MN+MS+SS-WeA7, 51
Song, Z.B.: SP+AS+MI+NS+SS-TuM12, 19
Sorescu, D.C.: SS+AS+MI-MoM4, 3; SS+EM+HC+MI-ThM5, 71
Spencer, S.J.: AS+MI+SS-TuM2, 12
Sperling, B.A.: 2D+EM+SS+TF-WeM2, 37
Sprowl, L.H.: HC+SS-TuA1, 25
Sriraman, S.: PS+NS+SS+TF-FrM5, 83
Stafford, L.: 2D+AS+SS-ThA7, 73; PS+AS+SS-MoA4, **7**
Stahl, D.: SP+AS+NS+SS-MoM4, 1
Stanford, M.G.: 2D+MI+NS+SS+TF-FrM8, **82**
Starostin, S.A.: PS+SS+TF-WeA3, 53
Staudt, S.: HC+SA+SS-WeA3, 49
Stavis, S.M.: NS+AS+EM+MI+SP+SS-ThM5, **66**
Steebins, D.: SS+AS+HC-MoA10, 10
Steinrück, H.-P.: SA+AS+HC+SS-TuA1, **30**
Stenger, B.H.: SS-WeM4, 46
Sterbinsky, G.E.: SA+AS+HC+SS-TuA9, 30
Stewart, M.D.: NS+MN+MS+SS-WeA2, 51; NS+MN+MS+SS-WeA3, 51
Stine, R.: 2D+BI+MN+SS-TuA1, 22
Strand, M.B.: AS+BI+SA+SS-ThM6, 61
Strandwitz, N.C.: TR+AS+HI+NS+SS-WeA2, 59
Stranick, S.J.: NS+AS+EM+MI+SP+SS-ThM12, 67
Strelcov, E.: SA+AS+HC+SS-WeA3, 54; SP+AS+NS+SS-MoM9, **2**
Stroscio, J.A.: MI+2D+AC+SA+SS-TuM2, 14
Strunskus, T.: SA+AS+HC+SS-WeA12, 55
Struzzi, C.: 2D+BI+MN+SS-TuA7, 22
Sturm, J.M.: SS-WeM6, **46**
Su, P.-H.: PS+NS+SS+TF-ThM10, 68
Sugano, R.: PS+NS+SS+TF-ThM12, 69
Sugawa, S.: SS-TuP21, 36
Sugawara, T.: SS+AS+EM-ThA9, 80
Suhartono, S.: EM+SS-TuA7, 24
Sumpter, B.G.: 2D+AS+SS-ThA6, 73; 2D+AS+SS-ThA9, 74
Sun, L.: SE+2D+NS+SS+TF-WeA3, **56**
Sun, T.: 2D+MI+NS+SS+TF-FrM9, 82
Sun, Z.: HC+NS+SS-WeM1, 40; SS+EM+HC+MI-ThM1, 71

Susi, T.: 2D+BI+MN+SS-TuA7, 22
Sutton, E.: NS+AS+EM+MI+SP+SS-ThM10, 66
Suzer, S.: AS+BI+SA+SS-ThM4, 61
Sykes, E.C.H.: HC+NS+SS-WeM13, **41**; HC+SA+SS-ThM5, 65; HC+SA+SS-WeA9, 50

— T —

Taga, R.: AS+BI+SA+SS-ThM10, **62**; AS+BI+SA+SS-ThM11, 62
Tait, S.L.: SS-TuP1, 34
Taj, S.: SS+HC-FrM5, 85
Takahashi, S.: HC+SA+SS-WeA1, 49
Takakuwa, Y.: AS+BI+SA+SS-ThM10, 62; AS+BI+SA+SS-ThM11, 62; SA+AS+HC+SS-WeA11, 55
Talukdar, T.K.: SS-TuP11, 35
Tamanaha, C.: 2D+BI+MN+SS-TuA1, 22
Tan, K.: SS+AS+HC-MoA6, **10**
Tan, S.: PS+NS+SS+TF-ThM3, 68
Tanabe, T.: HC+SA+SS-WeA1, 49
Tanaka, K.: SE+2D+NS+SS+TF-WeA4, 56; SE+PS+SS-ThM4, 69
Tanaka, S.: MN+BI+EM+SS+TR-TuM6, 16
Tang, C.: SS-TuP19, 36
Taniguchi, T.: MI+2D+AC+SA+SS-TuM2, 14
Tardio, S.: AS+SS-ThA8, **75**
Tassone, C.: HC+NS+SS-WeM2, 40
Tatsumi, T.: PS+AS+SS-MoA2, 6; PS+AS+SS-MoA9, 8
Tegenkamp, C.: SP+2D+AS+NS+SS-MoA5, **9**
Teichert, C.K.: SS-WeM10, 47
Tempas, C.: SS-TuP1, 34
Teplyakov, A.V.: SS+AS+MI-MoM9, **4**; SS+HC-FrM3, 85; SS-TuP15, 35; SS-TuP5, 34
Teramoto, A.: SS-TuP21, 36
Terfort, A.: 2D+EM+SS+TF-WeM10, 38; SS+AS+MI-MoM8, 3; SS+HC-TuM13, **21**
Terrones, M.: 2D+MI+NS+SS+TF-FrM7, 81
Terryn, H.: SS+AS+HC-MoA11, 11
Thelander, K.D.: NS+AS+EM+MI+SP+SS-ThM13, 67
Thiel, P.A.: SS+HC+NS-WeA7, 57
Thiel, R.: SP+AS+NS+SS-MoM4, 1
Thimsen, E.: PS+NS+SS-WeM3, 43
Thiry, D.: SE+PS+SS-ThM13, **70**
Thomas, A.: SS-WeM10, **47**
Thomas, S.: SS+AS+HC-MoA10, 10
Thonhauser, T.: SS+AS+HC-MoA6, 10
Thurmer, K.: SS+AS+MI-MoM3, 2
Tian, M.: 2D+AS+SS-ThA9, 74
Tian, P.: PS+SS-TuA11, 29
Timm, R.: NS+AS+EM+MI+SP+SS-ThM13, 67; SA+AS+HC+SS-TuA3, 30
Timokhin, I.G.: 2D+BI+MN+SS-TuA8, 22
Todoroki, N.: HC+SA+SS-WeA1, 49
Tomova, Z.: PS+AS+SS-MoA5, 7
Toomey, R.: SS+AS+HC-MoA10, 10
Torrea-Ochoa, A.: AS+MI+SS-TuM5, 12
Torres-Ochoa, J.A.: AS+MI+SS-TuM11, **13**
Trappen, R.: MI+2D+AC+SA+SS-TuM12, 15
Trenary, M.: HC+SA+SS-ThM2, 64; SS+HC-TuM3, **20**
Tringides, M.C.: SS+HC+NS-WeA7, 57; SS-WeM1, **46**
Troian, A.: SA+AS+HC+SS-TuA3, **30**
Troparevsky, M.C.: NS+MN+MS+SS-WeA7, 51
Trotochaud, L.: SS+AS+HC-MoA11, 11; SS+HC-TuM11, **21**
Tsai, P.: TR+AS+HI+NS+SS-WeA1, 59
Tselev, A.: SP+AS+NS+SS-MoM9, 2
Tsuchikawa, R.: NS+EM+MI+SS-TuM4, 17
Tsyshevsky, R.: SS+HC-TuM11, 21
Turano, M.E.: HC+SA+SS-WeA10, 50
Turchanin, A.: 2D+EM+SS+TF-WeM10, 38
Turkmen, Y.E.: AS+BI+SA+SS-ThM4, 61
Turner, K.T.: TR+AS+HI+NS+SS-WeA1, 59

— U —

Uedono, A.: PS+SS+TF-WeA1, 52
Uehara, S.: SS+AS+EM-ThA9, **80**
Ulgut, B.: AS+BI+SA+SS-ThM4, 61
Uner, N.B.: PS+NS+SS-WeM3, **43**
Uptrey, B.: NS+MN+MS+SS-WeA10, 52
Utz, A.L.: HC+SS-ThA3, **76**; SS+HC+NS-WeA11, 58

— V —

Vahedi, V.: PS+NS+SS+TF-ThM3, 68
Valbuena, M.: SS-WeM12, 47
Van Berkel, GJ.: AS+SS-ThA1, **74**
van de Kruijs, R.W.E.: SS-WeM6, 46
van de Sanden, M.C.M.: PS+SS+TF-WeA3, 53; PS+SS-TuA1, 28; PS+SS-TuA10, **29**; PS+SS-TuA4, 28
van der Velden-Schuermans, B.C.A.M.: PS+SS+TF-WeA3, 53
Van Haren, R.: EM+SS-TuA7, 24
Van Surksum, T.L.: PS+NS+SS-WeM11, **44**
Vandalon, V.: PS+SS-TuA4, 28
Vandervelde, T.E.: EM+MI+NS+SP+SS-ThM10, 63
Vaniapura, V.: SS+AS+EM-ThA7, 80
Vasco, E.: NS+SP+SS-ThA1, 77
Vasudevan, R.: SP+2D+AS+NS+SS-MoA11, **9**
Vazquez-Lepe, M.-O.: AS+MI+SS-TuM5, 12
Veillerot, M.: SA+AS+HC+SS-TuA10, 31
Ventrice, Jr., C.A.: 2D+EM+SS+TF-WeM11, 38
Ventzek, P.L.G.: PS+NS+SS+TF-FrM1, 82; PS+NS+SS+TF-FrM3, 83
Veyan, J.-F.: SS+AS+HC-MoA6, 10
Vianco, P.T.: AS+BI+MI+NS+SA+SS-WeM12, 39
Viani, M.: NS+SP+SS-ThA9, 78
Vidal, V.: SA+AS+HC+SS-TuA12, 31
Vinchon, P.: PS+AS+SS-MoA4, 7
Vinx, N.: SE+PS+SS-ThM13, 70
Vlasak, P.R.: AS+BI+MI+NS+SA+SS-WeM5, **39**
Vlassiouk, I.: 2D+AS+SS-ThA6, 73; NS+MN+MS+SS-WeA11, 52; SP+AS+NS+SS-MoM9, 2
Voevodin, A.A.: SE+2D+NS+SS+TF-WeA9, 57
Vogel, J.D.: SA+AS+HC+SS-WeA9, **55**
Voigt, B.: PS+NS+SS-WeM10, 44
Voigtländer, B.: SP+AS+NS+SS-MoM1, **1**
Vojvodic, A.: HC+NS+SS-WeM1, 40
von Borany, J.: NS+MN+MS+SS-WeA1, 50

— W —

Wachtel, E.: MN+BI+EM+SS+TR-TuM12, 16
Wächter, T.: SS+AS+MI-MoM8, 3
Wäckerlin, A.: SP+AS+MI+NS+SS-TuM4, 18
Wäckerlin, C.: SP+AS+MI+NS+SS-TuM4, 18
Wadayama, T.: HC+SA+SS-WeA1, **49**
Wadley, P.: SP+2D+AS+NS+SS-MoA3, 8
Wagenbach, C.: EM+SS-TuA9, 24
Walczak, L.: AS+SS-ThA10, **75**
Walker, A.V.: 2D+EM+SS+TF-WeM1, 37; AS+SS-ThA3, 74
Walkup, D.: MI+2D+AC+SA+SS-TuM2, 14
Wallace, R.M.: EM+SS-TuA12, 25
Wallin, C.B.: NS+EM+MN+PS+SS-TuA1, **26**
Walton, A.S.: HC+NS+SS-WeM1, 40
Walton, S.G.: PS+NS+SS+TF-FrM6, **83**
Waluyo, I.: AS+BI+SA+SS-ThM1, **61**; SS+HC-TuM6, 20
Wang, C.: NS+HC+SS-MoA2, 5; SS+AS+MI-MoM3, **2**
Wang, H.: SS+AS+HC-MoA6, 10
Wang, J.G.: AS+BI+MI+NS+SA+SS-WeM13, **40**
Wang, J.H.: SS+AS+MI-MoM10, 4
Wang, M.: PS+NS+SS+TF-FrM3, **83**
Wang, Q.: EM+SS-TuA12, 25
Wang, S.: PS+NS+SS+TF-ThM1, 67
Wang, T.: SS+HC-TuM2, 19
Wang, X.: NS+MN+MS+SS-WeA2, 51; NS+MN+MS+SS-WeA3, 51
Wang, Y.: NS+EM+MN+PS+SS-TuA8, **27**; NS+HC+SS-MoA5, 5
Warner, J.H.: 2D+AS+SS-ThA3, **73**
Waser, R.: SA+AS+HC+SS-WeA7, 54
Watanabe, K.: AS+SS-ThA9, 75
Watanbe, K.G.: MI+2D+AC+SA+SS-TuM2, 14
Weaver, J.F.: HC+SA+SS-ThM12, 65; SS+EM+HC+MI-ThM3, **71**; SS-TuP3, 34; SS-TuP6, 34
Webb, J.: NS+AS+EM+MI+SP+SS-ThM13, 67
Weber, B.: SP+AS+NS+SS-MoM10, 2
Weber-Bargioni, A.: 2D+BI+MN+SS-TuA9, 23
Wee, A.T.S.: SP+AS+MI+NS+SS-TuM12, **19**
Wei, D.H.: SS+AS+MI-MoM10, 4; SS+AS+MI-MoM5, **3**
Wei, R.: SE+PS+SS-ThM3, 69
Wei, Z.: NS+EM+MI+SS-TuM10, 17
Weiland, C.: SA+AS+HC+SS-TuA9, **30**
Weinstein, D.: MN+BI+EM+SS+TR-TuM3, **15**
Wen, Z.: SS+EM+HC+MI-ThM2, 71
Wendt, S.: SS+EM+HC+MI-ThM11, 72
Westberg, G.: EM+MI+NS+SP+SS-ThM13, 64
Westly, D.A.: NS+EM+MN+PS+SS-TuA1, 26
Westover, T.: NS+MN+MS+SS-WeA10, **52**
White, M.G.: HC+SA+SS-WeA11, **50**; SS+AS+HC-MoA5, 10
Whitelam, S.: SS-WeM3, 46
Whiteman, P.: NS+AS+EM+MI+SP+SS-ThM1, 65
Whitener, K.E.: 2D+BI+MN+SS-TuA1, **22**
Wickenburg, S.: 2D+BI+MN+SS-TuA9, 23
Wiesendanger, R.M.: NS+EM+MI+SS-TuM12, **18**
Wilhelm, F.: MI+2D+AC+SA+SS-TuM6, 15
Williams, M.G.: SS+HC-FrM3, **85**
Wilson, M.: TR+AS+HI+NS+SS-WeA2, 59
Wilson, N.S.: 2D+EM+SS+TF-WeM5, 37
Winarski, R.P.: NS+HC+SS-MoA5, 5
Wisman, D.: SS-TuP1, **34**
Wodtke, A.: HC+SS-ThA1, 76
Woicik, J.C.: SA+AS+HC+SS-TuA9, 30
Wolf, D.: NS+MN+MS+SS-WeA1, 50
Wong, T.: EM+MI+NS+SP+SS-ThM13, **64**
Wood, P.: SS+AS+EM-ThA9, 80
Woollard, S.: SE+PS+SS-ThM6, 70
Woolley, A.: NS+MN+MS+SS-WeA10, 52
Wu, B.: PS+SS+TF-WeA10, 53
Wu, C.: SS-TuP3, 34
Wu, W.: NS+EM+MN+PS+SS-TuA8, 27
Wyrick, J.: NS+MN+MS+SS-WeA2, 51; NS+MN+MS+SS-WeA3, **51**

— X —

Xiao, K.: 2D+AS+SS-ThA9, **74**
Xiao, Z.: SP+AS+MI+NS+SS-TuM3, 18
Xie, W.: PS+NS+SS+TF-FrM10, **84**
Xin, Y.: 2D+MI+NS+SS+TF-FrM4, 81
Xu, T.: SS+AS+MI-MoM6, 3
Xu, X.M.: NS+MN+MS+SS-WeA1, **50**

— Y —

Yakshin, A.E.: SS-WeM6, 46
Yamaguchi, Y.: PS+NS+SS+TF-ThM13, **69**
Yamazui, H.: AS+SS-ThA9, 75
Yang, C.: NS+EM+MI+SS-TuM11, 18
Yang, H.: MI+2D+AC+SA+SS-TuM3, **14**
Yang, J.Q.: SS-TuP20, 36
Yang, S.: 2D+BI+MN+SS-TuA8, 22
Yang, Z.: NS+HC+SS-MoA2, 5
Yarrington, C.D.: SE+2D+NS+SS+TF-WeA8, 56
Yasini, P.: SP+AS+MI+NS+SS-TuM1, **18**
Yazyev, O.V.: 2D+BI+MN+SS-TuA9, 23
Ye, Z.: TR+AS+HI+NS+SS-WeA3, 59
Yeom, G.Y.: PS+AS+SS-MoA3, 7; PS+NS+SS+TF-ThM6, 68; SE+PS+SS-ThM5, 70
Yngman, S.: SA+AS+HC+SS-TuA3, 30
Yoon, M.: 2D+AS+SS-ThA9, 74
Yoshida, N.: SS-TuP4, **34**; SS-TuP8, 35
Yoshigoe, A.: AS+BI+SA+SS-ThM11, 62; SA+AS+HC+SS-WeA11, 55
Youn, T.S.: SP+AS+MI+NS+SS-TuA1, 31
Yousefi Sarraf, S.: MI+2D+AC+SA+SS-TuM12, 15
Yu, D.: SE+2D+NS+SS+TF-WeA4, 56
Yu, X.F.: AS+BI+MI+NS+SA+SS-WeM1, 38
Yu, X.-J.: SS+HC-TuM13, 21

Yu, X.Y.: AS+BI+MI+NS+SA+SS-WeM1, 38;
  AS+BI+MI+NS+SA+SS-WeM13, 40
Yu, XY.: NS+AS+EM+MI+SP+SS-ThM2, **66**
Yu, Y.: SS+HC-TuM11, 21
Yuan, L.: TR+AS+HI+NS+SS-WeA3, 59
Yulaev, A.: SA+AS+HC+SS-WeA3, 54;
  SP+AS+NS+SS-MoM9, 2

— Z —

Żaba, T.: SS+AS+MI-MoM8, 3
Zabka, W.-D.: AS+BI+SA+SS-ThM12, 62
Zachariah, M.: SS+HC-TuM11, 21
Zahl, P.: SS+HC-FrM10, 86
Zanette, D.H.: MN+BI+EM+SS+TR-TuM5, 16
Zehnder, A.T.: NS+EM+MN+PS+SS-TuA1, 26
Zhang, C.: EM+SS-TuA12, 25
Zhang, D.Y.: HC+SA+SS-ThM3, 64
Zhang, F.: AS+BI+MI+NS+SA+SS-WeM1, 38
Zhang, H.: SA+AS+HC+SS-WeA1, 54
Zhang, Y.: 2D+BI+MN+SS-TuA9, 23;
  AS+BI+MI+NS+SA+SS-WeM13, 40;
  PS+NS+SS+TF-FrM5, 83;
  TR+AS+HI+NS+SS-WeA11, **59**
Zhang, Z.: HC+NS+SS-WeM5, **41**; SS-TuP11, **35**
Zhang, Z.Y.: NS+EM+MI+SS-TuM4, 17
Zhao, J.: SS-TuP15, **35**
Zhao, W.: HC+SS-ThA10, **77**
Zharnikov, M.: SS+AS+MI-MoM8, 3
Zheng, J.: PS+SS-TuA10, 29
Zheng, W.: NS+EM+MN+PS+SS-TuA2, 26
Zheng, Y.J.: SP+AS+MI+NS+SS-TuM12, 19
Zhitenev, N.B.: MI+2D+AC+SA+SS-TuM2, 14;
  SP+AS+NS+SS-MoM9, 2
Zhou, C.: SS+HC-TuM12, 21
Zhu, H.: EM+SS-TuA12, **25**
Zhu, J.F.: SS+HC-TuM2, **19**
Zhu, Z.H.: AS+BI+MI+NS+SA+SS-WeM1, 38;
  AS+BI+MI+NS+SA+SS-WeM13, 40;
  NS+HC+SS-MoA2, 5
Zhuang, J.-L.: SS+HC-TuM13, 21
Zielasek, V.: SS-TuP6, 34
Zou, J.: NS+EM+MN+PS+SS-TuA3, 27
Zou, Q.: SP+2D+AS+NS+SS-MoA10, **9**
Zuluaga, S.: SS+AS+HC-MoA6, 10