Electronic Materials and Photonics
Room 102A - Session EM+NS+PS+SS+TF-MoM

Growth and Devices Technology of Group III-Nitrides

Moderators: Nikolaus Dietz, Georgia State University, Shalini Gupta, Northrop Grumman ES

8:20am **EM+NS+PS+SS+TF-MoM1 Development of AlGaN based UV Laser Diodes***, **Ronny Kirste**,* Adroit Materials*; B. Sakar, A. Franke,* NCSU*; J. Tweedie,* Adroit Materials*; Z. Bryan, I. Bryan,* NCSU*; S. Mita,* Adroit Materials*; R. Collazo, Z. Sitar,* NCSU **INVITED**

UV laser diodes are widely desired for many important applications such as chemical and biological sensing, non-line of sight communications, and DNA tagging. Design and fabrication of AlGaN based laser diodes is the most promising pathway for next generation UV lasers but challenges for these devices are many including low n- and p-conductivity, absorbing injection layers, and non-ohmic contacts. Here, we present recent advances in the growth and fabrications of UV laser diodes. The presentation will cover the most important steps that are necessary to achieve electrically injected UV laser diodes. These include: AlGaN epitaxy, doping, fabrication, and design.

As an advancement over most existing approaches, we pursue the growth of our device structures on single crystalline AlN substrates which allows for low dislocation densities < 10^4 cm^2. Any such device fabrication is started with the growth of an AlN homoepitaxial layer. It is demonstrated that this epitaxial layer can be grown with a dislocation density that follows that of the substrate and no interface between layer and substrate is observed in TEM, which indicates true homoepitaxy. Subsequent growth of AlGaN layers with Al content ranging 50-85% is shown to be pseudomorphic. An excellent control of the AlGaN surface morphology is demonstrated using a supersaturation scheme and bilayer steps as needed for highly efficient MQWs are achieved. MQWs for emission at wavelengths ranging 240-280 nm are discussed and optically pumped lasing in this region is demonstrated. The chosen approach to grow on AlN is validated by realizing MQWs with an IQE exceeding 90%. In order to achieve electrically injected UV lasing, Al-rich AlGaN is doped and free electron concentrations for the n-cladding with 80% Al-content is shown to be around $8x10^{18}$ cm^{-3}. In contrast, p-doping of AlGaN is much more challenging because of the high activation energy of the Mg acceptor. Consequently, achievable free hole concentration and conductivity of the p-cladding are low. We discuss how these epitaxial layers can be used for realizing laser diodes. Experimental work is supported by simulations and used to direct the UV laser design. Finally, we present electrical data and electroluminescence spectra from fully fabricated diodes and discuss the future challenges that need to be addressed to demonstrate the first electrically injected UV laser diode.

9:00am **EM+NS+PS+SS+TF-MoM3 Low-Temperature PA-ALD Growth Technology for Group III-Nitride Nano-heterostructures and their (Opto)Electronic Device Applications***, **Necmi Biyikli**, A. Haider, S. Kizir, P. Deminskyi, M. Yilmaz, S. Bolat, A. Celebioglu, A.K. Okyay, T. Uyar,* Bilkent University, Turkey*; F. Buyukserin, S. Altuntas,* TOBB University of Economics and Technology, Turkey*; I. Yilmaz, K. Khaled,* Turgut Ozal University, Turkey **INVITED**

Being initially developed for an entire different area of use, atomic layer deposition (ALD) became a widespread tool to grow functional films and conformal ultra-thin coatings for numerous applications. Based on self-limiting surface reactions, ALD enabled the low-temperature growth of various materials including dielectrics, semiconductors, and metals. Featuring the capability to deposit wafer-scale uniform semiconductor films at relatively low-temperatures with sub-monolayer thickness control and ultimate conformality makes ALD attractive for the semiconductor community. Towards this end, precursors and growth recipes are developed to deposit crystalline thin films for compound and elemental semiconductors. Conventional thermal ALD techniques as well as plasma-assisted and radical-enhanced ALD techniques have been exploited to achieve decent film quality compatible with device applications.

In this presentation, we give an overview of our research efforts on plasma-assisted ALD-based nanoscale semiconductor research focusing on III-nitrides. We have combined our low-temperature thin-film growth recipes with various nanoscale templates and exploited the conformality feature of ALD technique to fabricate nitride nanostructures. Electrospun polymeric nanofibers have been used to produce flexible polymer/III-nitride core-shell structures which might be used for flexible optoelectronics. In addition, hollow-core multi-shell III-nitride nano-heterostructures are demonstrated as well. Anodized alumina (AAO) templates were utilized to fabricate large-area ordered III-nitride nanostructures including radial heterostructures. Extensive growth and fabrication recipe development and materials characterization details will be presented.

The synthesized III-nitride nanoscale semiconductor materials might find applications in a vast amount of applications including physical and chemical sensing, piezo-electric energy harvesting, photocatalysis, nanoscale and flexible (opto)electronics. As proof-of-principle device demonstrations, we have shown nanofibrous GaN/InN-based photocatalysis, GaN/InN-based chemical (gas) sensing, and nanoscale GaN-based UV photodetectors.

9:40am **EM+NS+PS+SS+TF-MoM5 Structural Qualities of GaN Grown on AlN Buffer Layer by MEPA-MOCVD***, **Daniel Seidlitz**, I. Senevirathna, A. Fali, Y. Abate, N. Dietz,* Georgia State University*; A. Hoffmann,* Technical University Berlin, Germany

This study focusses on the influence of Aluminum nitride (AlN) buffer layers on the structural and optoelectronic properties of subsequent overgrown Gallium nitride (GaN) layers, using Migration Enhanced Plasma-Assisted Metal Organic Chemical Vapor Deposition (MEPA-MOCVD).

One challenge in group-III nitride growth is the lattice mismatch between the substrate (e.g. sapphire (Al_2O_3), silicon or silicon carbide) and the group III-Nitride layer as for example GaN. Lattice mismatch imposes compressive strain/stress and influences the crystal quality of subsequent grown group-III nitrides. Inserting an AlN interlayer between the sapphire substrate and the GaN epilayer, transitions the oxygen surface chemistry to a nitrogen surface chemistry, separating surface chemistry related defects from lattice mismatch induced defects, which leads to an improved crystalline quality of the overgrowning GaN layer.

All group III-Nitride layers are grown on sapphire substrates using MEPA-MOCVD. The system design allows the growth of GaN at lower temperatures by using plasma activated nitrogen species (N*/NH*/NHx*) as nitrogen precursor, which are generated by a radio-frequency hollow cathode plasma source (MEAglow^{TM}) scalable from 20W up to 600W. The tunable nitrogen plasma source enables to control the kinetic energies of the active nitrogen species in the afterglow region to be directed at the growth surface, where they interact with metalorganic (MO) precursors. The growth process parameter set includes: reactor pressure, growth temperature, pulsed injection of MO- and nitrogen plasma fluxes, plasma species and their energies.

The structural properties of the AlN buffer layers (e.g. local ordering, grain size, surface topography) are analyzed by Atomic Force Microscopy (AFM) and Raman spectroscopy. The film thickness and optoelectronic properties of the AlN and GaN layers are studied Fourier Transform infrared (FTIR) and reflectance spectroscopy. Results are presented on the structural and optoelectronic properties of the GaN layers as function of the process parameters and the properties of the underlying AlN buffer layer.

10:00am **EM+NS+PS+SS+TF-MoM6 Optical and Electrical Characteristics of Gamma-ray Irradiated AlGaN/GaN Heterostructures***, **MinPrasad Khanal**, B. Ozden, K. Kim, S. Uprety, V. Mirkhani, L. Shen, K. Yapabandara, A.C. Ahyi, M. Park,* Auburn University

AlGaN/GaN high electron mobility transistors (HEMTs) show their potential immunity toward high energy radiation related damages, making them promising candidates for the radiation hard electronics. The degradation in performance of these devices under radiation exposed environment might be due to different possible effects in the device structure such as strain/stress, generation of dislocation, carrier removal and reduction in two-dimensional-electron-gas (2DEG) concentration.The AlGaN/GaN epi structures grown on 6 inch Si wafer were used and irradiated with 120 MRad doses of gamma-ray produced from ^{60}Co source. The semi-transparent (with 10-15 nm thickness) Ni Schottky diodes and circular HEMT devices were fabricated using un-irradiated and gamma-ray irradiated AlGaN/GaN epi structures. In the case of HEMT devices, Ti/Al/Ni (30/180/40 nm thickness) for the ohmic contact and Ir (15 nm thickness) for the gate contact formation were deposited using dc magnetron sputtering system. Spectroscopic photo current-voltage (IV) measurements both with sub-band gap and above band-gap illumination, micro-Raman/photoluminescence spectroscopy, and transistor characterizations were performed. The spectroscopic photo IV measurements were carried out by applying the variable wavelength ultra-violet (UV) and visible light from Xenon lamp source under reverse bias condition. Sub-bandgap illumination (800 nm-400 nm) provided the information about sub-bandgap energy levels of defects by relating the change in photocurrent level in response to the applied light spectrum. On the other hand, above bandgap illumination (280 nm-400 nm) utilizes the fact that the penetration depth of a light varies as a function of wavelength. The result showed reduction in photocurrent on the gamma-ray irradiated samples in comparison to the un-irradiated samples, revealing the possibility of creation of extra defects, and hence, decreasing the carrier concentration in the 2DEG. Micro-Raman and photoluminescence (PL) spectroscopic analysis on both the samples were also performed and the results show no substantial change in their spectra, supporting the conclusion from previous scientific reports of radiation resistance of the HEMTs on their bulk structure level. Decrease in drain current and transconductance were observed from the transistor IV measurements, indicating a possible reduction in carrier concentration. It can be concluded that the reduction on photocurrent, drain current level and transconductance after the gamma-ray irradiation are due to the possible creation of some extra defects and decrease of carrier concentration on 2DEG channel.

10:40am **EM+NS+PS+SS+TF-MoM8 Seeded Regrowth for Production of AlN and GaN Substrates by HVPE**, ***Jacob Leach***, *K. Udwary, G. Dodson, K. Gentry, P. Quayle, T. Schneider, H. Splawn, K. Evans,* Kyma Technologies, Inc. **INVITED**

Freestanding GaN and freestanding AlN remain the substrates of choice for the highest performing vertical high voltage switching devices (>1200V) and UV optoelectronics, respectively. However, the cost of these substrates remains high, availability remains low, and the crystalline quality of these substrates varies depending on the growth technique employed. In particular, the electrical quality of GaN substrates and the UV transparency of AlN substrates depend on the specific growth conditions utilized and it remains a challenge to maintain high crystalline quality while simultaneously realizing high electrical quality or UV transparency. We proposed the use of hydride vapor phase epitaxy (HVPE) as a cloning technique to replicate the high crystalline quality of existing solvothermally grown GaN or physical vapor transport (PVT) grown AlN substrates while maintaining high electrical and optical quality. In this talk, we report Kyma's recent results in the use of the HVPE replication technique for realizing both AlN and GaN substrates.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-MoM

Advances in Scanning Probe Microscopy

Moderators: Saban Hus, Oak Ridge National Laboratory, Chanmin Su, Bruker Nano

8:20am **SP+AS+MI+NS+SS-MoM1 Ultrafast Imaging of Polarization Switching in Ferroelectrics via Complete Information Acquisition in SPM**, ***Suhas Somnath***, *A. Belianinov, S.V. Kalinin, S. Jesse,* Oak Ridge National Laboratory

SPM imaging can be represented as an information channel between the dynamic processes at the tip-surface junction and the observer. Current SPM techniques use heterodyne detection methods such as lock-in amplifiers which result in significant loss in vital information such as information from higher eigenmodes, mode-mixing, and other non-linear phenomena in the tip-surface interaction. We present a new technique called General-mode (G-mode) where we capture the complete broad-band response of the cantilever at sampling rates of 1-100 MHz. The availability of the complete cantilever response facilitates the application of various physical models as well as multivariate statistical methods to extract information that has been unavailable from current SPM techniques. 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 highly sensitive to the local defects and structural imperfections at the micro and nanometer scale, which have undesirable effects on ferroelectric domains. These considerations necessitated the development of Piezoresponse Force Microscopy (PFM) imaging and spectroscopy techniques to measure and manipulate local polarization states. However, the current state-of-art PFM spectroscopy techniques suffer from serious compromises in the measurement rate, measurement area, voltage and spatial resolutions since they require the combination of a slow (~ 1 sec) switching signal and a fast (~ 1 – 10 msec) measurement signal. Furthermore, these techniques only capture the narrow-band cantilever response. We report on a fundamentally new approach that combines the full cantilever response from G-mode with intelligent signal filtering techniques to directly measure 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. The improved measurement speed enables dense 2D maps of material response with minimal drift in the tip position.

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.

8:40am **SP+AS+MI+NS+SS-MoM2 Development of Synchrotron X-ray Scanning Tunneling Microscopy**, ***Nozomi Shirato,*** Center for Nanoscale Materials at Argonne National Laboratory; *H. Chang,* Ohio University; *M. Cummings,* Advanced Photon Source at Argonne National Laboratory; *S.W. Hla,* Center for Nanoscale Materials at Argonne National Laboratory; *V. Rose,* Advanced Photon Source at Argonne National Laboratory

Advancements of scanning probe microscopy have been contributing to broaden fundamental understating of surface physics. By combining high intense X-ray beam as a probe and a functionalized tip as a detector, synchrotron X-ray scanning tunneling microscopy has been developed in Advanced Photon Source at Argonne National Laboratory. The recent studies demonstrated the technique has capabilities to extract chemical information with sensitivity at the atomic limit [1] and localized magnetic contrast by utilizing polarized beams [2]. Furthermore, at Argonne, in order to fully exploit potentials of the microscope, a dedicated beamline is under construction. The soft X-ray beamline has the energy range of 400 to 1600 eV and is equipped with a polarizer and focusing optics. The capabilities of the beamline will benefit the communities to explore chemical, magnetic and electronic properties of materials at atomic resolution.

References

[1] N. Shirato et al., Nano Letters 14, 6499 (2014).

[2] A. DiLullo et al., J. Synchrotron Rad. 23, 574 (2016).

9:00am **SP+AS+MI+NS+SS-MoM3 Development and Integration of a Universal SPM head: Design Criteria and Challenges**, *B. Guenther,* Sigma Surface Science GmbH, Germany; *J. Hilton,* Mantis Deposition; *A. Feltz,* Sigma Surface Science GmbH; ***Andreas Bettac,*** Sigma Surface Science GmbH, Germany

Recently we have developed an SPM microscope head that merges the needs for high resolution STM/QPlus[1]-AFM and at the same time satisfies the requirements for integration into different cryogen environments including tip and sample handling.

The new SPM head was integrated into different platforms, e.g. in a UHV Helium Flow Cryostat system for temperatures <10K and in a ^{3}He Magnet Cryostat UHV system for high magnetic fields (±12T) and temperatures <400mK.

This contribution focuses on design aspects and challenges for the new SPM head with respect to spatial restrictions, sample sizes/standards, QPlus and STM signal shielding as well as on first results (STM, STS and QPlus) obtained with the different instrumental setups.

[1] F. J. Giessibl, Applied Physics Letters 73 (1998) 3956

9:20am **SP+AS+MI+NS+SS-MoM4 How Soft Is a Protein? Stress-Strain Curve of Antibody Pentamers with 5 pN and 50 pm Resolutions**, ***Alma Perrino****[*], Instituto de Ciencia de Materiales de Madrid, CSIC, c/ Sor Juana Ines de la Cruz 3, 28049 Madrid, Spain; *R. Garcia,* Instituto de Ciencia de Materiales de Madrid, CSIC,, Spain

Understanding the mechanical functionalities of complex biological systems requires the measurement of the mechanical compliance of their smallest components. Here, we develop a force microscopy method to quantify the softness of a single antibody pentamer by measuring the stress-strain curve with force and deformation resolutions, respectively, of 5 pN and 50 pm [1]. The curve shows three distinctive regions. For ultrasmall compressive forces (5-75 pN), the protein's central region shows that the strain and stress are proportional (elastic regime). This region has an average Young modulus of 2.5 MPa. For forces between 80 and 220 pN, the stress is roughly proportional to the strain with a Young modulus of 9 MPa. Higher forces lead to irreversible deformations (plastic regime). Full elastic recovery could reach deformations amounting 40% of the protein height. The existence of two different elastic regions is explained in terms of the structure of the antibody central region. The stress-strain curve

---

[*] **NSTD Student Award Finalist**

explains the capability of the antibody to sustain multiple collisions without any loss of biological functionality.

[1] Alma P. Perrino and R.Garcia. How soft is a protein? Stress-Strain curve of antibody pentamers with 5 pN and 50 pm resolutions. *Nanoscale,* 10.1039/C5NR07957H (2016)

9:40am **SP+AS+MI+NS+SS-MoM5 AVS Medard W. Welch Award Talk: Action Spectroscopy: Characterizing Molecules at Surfaces and its Dynamics***, **Maki Kawai***[*]*,* Institute for Molecular Science, Japan*; Y. Kim,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan*; K. Motobayashi,* Nagoya Institute of Technology, Japan*; H. Ueba,* Toyama University, Japan **INVITED**

STM is a useful tool for spectroscopy utilizing its ultimate spatial resolution. Electronic and vibrational information that STS and inelastic electron tunneling spectroscopy (IETS) carries is not only the reflection of the static spectroscopic information but also related to dynamical phenomena as motion or reaction of molecules induced by the excitation of molecular states. Action spectroscopy is the method to related the action of molecules induced and is utilized to identify the quantum states of the molecules. Dynamical information includes as how molecular vibrations can couple with the relevant dynamical processes [1,2]. I will present typical eamples of how the fundamental excitation of vibration modes is coupled with chemical reactions at surfaces.

References:

[1] Y. Kim, K. Motobayashi, T. Frederiksen, H. Ueba and Maki Kawai, Profress in Surface Science 90 (2015) 85-143, and the references within.

[2] K. Motobayashi, Y. Kim, M. Ohara, H. Ueba and Maki Kawai, Surf. Sci. 634 (2016) 18-22.

10:40am **SP+AS+MI+NS+SS-MoM8 Near-Field Spectroscopy and Imaging of Single Nanoparticles***, **Yohannes Abate**, D. Seidlitz, A. Fali, S. Gamage, V.E. Babicheva, V.S. Yakovlev, M.I. Stockman,* Georgia State University*; R. Collazo, D. Alden,* North Carolina State University*; N. Deitz,* Georgia State University **INVITED**

We investigate nanoscale phase separation on single InGaN QDs and nanostructures by using high-resolution s-SNIN (scattering type scanning near-field infrared nanoscopy) technique in the mid-IR spectral region. We fabricated patterned nanolayers down to few atomic layers thick that allow determination of the near-field infrared response of InGaN/InN/GaN heterostructures quantitatively. We first calibrate the near-field IR amplitude contrast as a function of composition and thickness of the semiconductor nanolayers and QDs. We then use this quantitative leads to identify phase separation in single QDs. An advanced theoretical model is developed to guide the experimental results. Unlike previous models that consider the probe conical tip as approximate point dipoles or spheroids, our model considers the full geometry of the tip and all the sample and substrate layers.

11:20am **SP+AS+MI+NS+SS-MoM10 Atomically-resolved Three-dimensional Structures of Electrolyte Aqueous Solutions near a Solid Surface***, **Daniel Martin-Jimenez**, E. Chacon,* Instituto de Ciencia de Materiales de Madrid, CSIC, Spain*; P. Tarazona,* IFIMAC Condensed Matter Physics Center, UAM, Spain*; R. Garcia,* Instituto de Ciencia de Materiales de Madrid, CSIC, Spain

Atomic-resolution three-dimensional images of electrolyte solutions near a mica surface demonstrate the existence of three types of interfacial structures [1-3]. At low concentrations (0.01-1 M), cations are adsorbed onto the mica until charge neutrality is reached. The cation layer is topped by a few hydration layers while anions are excluded from the mica surface [4]. At higher concentrations, the interfacial layer extends several nanometers into the liquid. It involves the alternation of cation and anion planes. Classical Fluid Density Functional calculations show that water molecules are a critical factor for stabilizing the structure of the ordered interfacial layer. The interfacial layer compatibilizes a crystal-like structure with liquid-like ion and solvent mobilities. At saturation, some ions precipitate and small ionic crystals are formed on the mica. The three-dimensional images have been acquired at 300 K.

[1] E. T. Herruzo, H. Asakawa, T. Fukuma, and R. Garcia, *Nanoscale* **5**, 2678-2685 (2013).

[2] K. Kobayashi *et al.The Journal of Chemical Physics* **138**, 184704 (2013)

[3] T. Fukuma *et al.Physical Review B* **92**, 7 (2015).

[4] M. Ricci, P. Spijker and K. Voitchovsky *Nat. Commun.* **5**, 4400 (2014).

11:40am **SP+AS+MI+NS+SS-MoM11 Super-resolution Optical and Chemical Imaging of Organic Thin Films using Tip-enhanced Near-Field Optical Microscopy***, A.L. Heilman, R. Hermann, **Michael Gordon**,* University of California at Santa Barbara

Sub-diffraction-limited (super-resolution) optical and chemical characterization of organic surfaces using a custom-built tip-enhanced near-field optical microscope with side-on and attenuated total reflectance (ATR) excitation and collection will be discussed. ATR illumination is combined with an Au optical antenna tip to show that (i) the tip can quantitatively transduce the optical near-field (evanescent waves) above the surface by scattering photons into the far-field, (ii) the ATR geometry enables excitation and characterization of surface plasmon polaritons (SPPs), whose associated optical fields can enhance Raman scattering from coumarin-6 (C6) and copper phthalocyanine (CuPc) films, and (iii) SPPs can be used to plasmonically excite the tip for super-resolution chemical imaging of patterned C6 and CuPc via tip-enhanced Raman spectroscopy (TERS). ATR-illumination TERS is quantitatively compared with the more conventional side-on illumination scheme using both experiment and FDTD optical simulations. In both cases, spatial resolution was better than 40 nm and tip on/tip off Raman enhancement factors were >6500. ATR illumination was shown to provide similar Raman signal levels at lower 'effective' pump powers due to additional optical energy delivered by SPPs to the active region in the tip-surface gap. Additional observations, such as the distance scaling of Raman enhancement and inelastic scattering generated by the plasmonic tip, as well as tip-enhanced photoluminescence imaging of patterned phthalocyanine films at spatial resolutions better than 20-30 nm, will be presented.

Surface Science
Room 104E - Session SS+AS+HC-MoM

Mechanistic Insights on Surface Reactions in Catalysis and at Novel Interfaces

Moderator: Bruce D. Kay, Pacific Northwest National Laboratory

8:20am **SS+AS+HC-MoM1 Study of Metal-Organic Complexation at Metal and Metal Oxide Surfaces by HREELS***, **Miao Wang**, C. Williams, S.L. Tait,* Indiana University

The ordering of organic molecules at surfaces and the formation of ordered metal nanostructures at surfaces have been extensively studied for the advancement of organic photovoltaics, nanoscale molecular electronics, and catalysts. There are many chemical systems that benefit from the combination of organic ligands with single-site metal centers to design and tune specific chemistries, but metal-organic complexation at surfaces has not yet been significantly studied. Molecular ligands on a surface with specific binding pockets can bind metal centers to achieve uniform oxidation states, as has been shown in prior studies by our group and by other groups. The goal of these studies is to improve selectivity in heterogeneous catalysts and to develop other novel surface chemistries. With that end in mind, we present new experiments with metal-organic coordination on oxide support surfaces. Most of the metal-organic surfaces studies have been done on metal surfaces to facilitate surface analysis. We have studied the redox assembly of 3,6-Di-2-pyridyl-1,2,4,5-tetrazine (DPTZ) and Pt on oxide surfaces, including rutile $TiO_2(110)$ using High Resolution Electron Energy Loss Spectroscopy (HREELS), Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED). HREELS characterizes vibrational modes, which can provide key information about adsorbate interactions and metal-organic interactions at surfaces. DPTZ and Pt were sublimated onto the surface from a Knudsen-type evaporator. Submonolayer DPTZ vibrational modes were observed on Ag(111) (C-H bending modes at 400 cm^{-1}, 618 cm^{-1} and 772 cm^{-1}; ring deformation modes at 966 cm^{-1}, 1145 cm^{-1} and 1354 cm^{-1}) and on $TiO_2(110)$ (a ring deformation mode at 1580 cm^{-1} and a C-H stretching mode at 3060 cm^{-1}). To see the vibrational modes of adsorbates on TiO_2, a Fourier deconvolution technique was applied to remove multiple excitations of surface phonon. Annealing DPTZ on Ag(111) at 170 °C caused significant changes to the HREEL spectra (C-H bending modes at 400 cm^{-1} and 740 cm^{-1}, ring deformation modes at 1100 cm^{-1}, 1445 cm^{-1}, 1574 cm^{-1}, a C-H stretching mode at 3080 cm^{-1}), but no observable changes were seen for DPTZ on $TiO_2(110)$ until the sample was annealed at 290 °C. Adding equimolar Pt onto submonolayer DPTZ on Ag(111) caused similar vibrational changes to be observed, but at a lower temperature of 140 °C. HREELS studies of the Pt-DPTZ complex on $TiO_2(110)$, Au(100), and other surfaces are ongoing. By studying the redox assembly of metal-organic

---

[*] **Medard W. Welch Award Winner**

complexes on these surfaces, strategies can be developed to customize and tune the reactivity of novel surface catalysts.

8:40am **SS+AS+HC-MoM2 Studies of Single-site Catalysts on Powdered Oxide Support through Redox Assembly**, ***Linxiao Chen**, J.P. McCann, S.L. Tait,* Indiana University

High levels of reaction selectivity for selective alkane functionalization are generally difficult to achieve with metal nanoparticle heterogeneous catalysts, due to the variety of metal biding sites available. Motivated by the desire towards the development of uniform single-site metal centers at surfaces, our group has been working on the redox assembly of metal-organic systems at surfaces. On a single crystal gold surface, electrons are transferred from platinum to the ligand 3,6-Di-2-pyridyl-1,2,4,5-tetrazine (DPTZ). Utilizing this unique redox chemistry, long-range ordered 1D chains with an alternating metal-ligand structure were assembled at deposition of DPTZ with pre-adsorbed metallic platinum. All platinum sites are oxidized into Pt(II), and stabilized in the binding pocket between two DPTZ with identical chemical environment. Here, aiming at practical applications in catalysis, a novel solution-phase synthetic strategy was developed based on wet impregnation approach, in attempt to reproduce the similar metal-ligand structure on high-surface-area powdered oxide catalyst supports. X-ray photoelectron spectroscopy verified that the redox chemistry is applicable to real supports, and is crucial in the successful deposition of DPTZ despite a weak ligand-support interaction. The surface structure is further elucidated by X-ray diffraction and surface titration. It was concluded that the mobility of the metal and ligand on a rough support surface, and the existence of residual Cl from Pt precursors represent major challenges. This metal-ligand structure can be manipulated by tuning strength of interaction between the supports, metal and ligand. Initial catalytic tests with the methane oxidation reaction exhibited C-H activation ability and selectivity similar to traditional highly-dispersed Pt catalysts. We have compared these catalysts and explored the limitations of single-site metal-organic complexes at oxide supports. Though being significantly stabilized by the favored coordination geometry and the redox chemistry, the thermal stability of the metal-ligand structure needs to be further enhanced.

9:00am **SS+AS+HC-MoM3 Controlled Reactions of Coordination Complexes on Oxide Surfaces**, ***Susannah Scott,*** University of California at Santa Barbara **INVITED**

The reactions of coordination complexes with functional groups on oxide surfaces (acidic and basic hydroxyl groups, Lewis acidic cations and Lewis basic oxide anions) can lead to anchored metal complexes with a high degree of uniformity when conducted under carefully controlled conditions (low-to-moderate temperatures, absence of moisture and/or O_2). Detailed characterization of these sites using spectroscopic methods, elemental analysis and reactivity studies leads to information about their structure and insight into the underlying structure of the oxide surface. Experiments with gold and silver complexes such as $Me_2Au(acac)$ and Ag(acac) reveal that interactions with surface hydroxyls involving strong H-bonding to ligand donor atoms are primarily responsible for their dispersion as isolated metal sites. By modulating the hydroxyl density via thermal pretreatment, it is possible to control not only the surface density of metal atoms, but also their subsequent mobility. In the case of nucleation and subsequent autocatalytic growth of metal nanoparticles, it is possible to exert control over particle size via the initial metal complex-oxide surface interaction.

9:40am **SS+AS+HC-MoM5 Adsorption and Activation of CO_2 on Cu(997) at Low Temperature**, ***Jun Yoshinobu,*** The University of Tokyo, Japan

Adsorption and activation of carbon dioxide on Cu(997) were investigated by infrared reflection absorption spectroscopy (IRAS), temperature programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS). CO_2 molecules are *physisorbed* on Cu(997) at temperatures below 70 K. However, the vibrational spectra of adsorbed CO_2 depend significantly on the substrate temperature; IR spectra of CO_2 vibrational modes at 70 K show asymmetric Fano line shapes. On the other hand, at 85 K, the dissociation of CO_2 into CO was observed on Cu(997) by IRAS and XPS, but not on Cu(111). In addition, the reaction of CO_2 on Cu(997) surface at 340 K under CO_2 gas pressure of 0.8 mbar was investigated by ambient pressure XPS. A main reaction product on the surface was identified as carbonate (CO_3), based on estimation of the composition ratio of oxygen to carbon. CO_3 was produced on the surface through the reaction of CO_2 with atomic oxygen formed from CO_2 dissociation.

10:00am **SS+AS+HC-MoM6 D_2O Interaction with Planar ZnO(0001) Bilayer Supported on Au(111): Structures, Energetics and Influence of Hydroxyls**, ***Xingyi Deng**, D.C. Sorescu, J. Lee,* National Energy Technology Laboratory

Ultrathin oxides with single or few atomic layers are considered new types of due to the emergence of film-specific structures with properties distinct from their bulk counterparts. ZnO(0001) bilayer grown on Au(111) adopts a planar, graphite-like structure via an intralayer relaxation from the bulk wurtzite structure. In this work, we investigate the interaction between D_2O and the planar ZnO(0001) bilayer grown on Au(111) with temperature programed desorption (TPD), low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) calculations. D_2O molecules adsorbed on this planar surface form two ordered overlayers, a (3 × 3) and a $(\sqrt{3} \times \sqrt{3})R30^\circ$, not seen before on any of the bulk ZnO single crystal surfaces. The apparent activation energies of desorption (E_d) estimated from TPD peaks agree well with the adsorption energy values calculated from DFT. The DFT calculations also reveal that both overlayers are mediated by extensive hydrogen bonding among the molecules but with different packing densities. The hydroxyl groups, accumulating very slowly on the ZnO(0001) bilayer surface under the standard ultrahigh vacuum (UHV) environment, strongly suppress the formation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer but have less impact on the (3 × 3) overlayer. We suggest that the difference in packing densities of the overlayers leads to these findings such that only the (3 × 3) overlayer with a more open structure can accommodate small amounts of the adsorbed hydroxyls.

10:40am **SS+AS+HC-MoM8 Nanoscale Silicon as a Catalyst for Graphene Growth: Mechanistic Insight from In-Situ Raman Spectroscopy**, ***Keith Share**, R.E. Carter,* Vanderbilt University*; P. Nikolaev, D. Hooper,* Air Force Research Laboratory*; L. Oakes, A.P. Cohn,* Vanderbilt University*; R. Rao,* Air Force Research Laboratory*; A.A. Puretzky,* Oak Ridge National Lab*; D.B. Geohegan, B. Maruyama,* Air Force Research Laboratory*; C.L. Pint,* Vanderbilt University

Nanoscale carbons are typically synthesized by thermal decomposition of a hydrocarbon at the surface of a metal catalyst. Whereas the use of silicon as an alternative to metal catalyst could unlock new techniques to seamlessly couple carbon nanostructures and semiconductor materials, stable carbide formation in bulk silicon prevents the precipitation and growth of graphitic structures. Here, we provide evidence supported by comprehensive *in-situ* Raman experiments that indicates nanoscale grains of silicon in porous silicon (PSi) scaffolds act as catalysts for hydrocarbon decomposition and growth of few-layered graphene at temperatures as low as 700 K. Self-limiting growth kinetics of graphene with activation energies measured between 0.32 – 0.37 eV elucidates the formation of highly reactive surface-bound Si radicals that aid in the decomposition of hydrocarbons. Nucleation and growth of graphitic layers on PSi exhibits striking similarity to catalytic growth on nickel surfaces, involving temperature dependent surface and subsurface diffusion of carbon. This work elucidates how the nanoscale properties of silicon can be exploited to yield catalytic properties distinguished from bulk silicon, opening an important avenue to engineer catalytic interfaces combining the two most technologically-important materials for modern applications – silicon and nanoscale carbons.

11:00am **SS+AS+HC-MoM9 Functionalization of Graphene on Ru(0001) with Atomic Oxygen**, ***Zbynek Novotny,*** Pacific Northwest National Laboratory*; F.P. Netzer,* Karl-Franzens University, Austria*; Z. Dohnálek,* Pacific Northwest National Laboratory

Well-defined, monodispersed catalysts supported on oxidized carbon nanotubes are a promising class of new materials for heterogeneous catalysis. While such systems exhibit lower complexity compared to traditional catalysts, many questions, such as the reproducible preparation of carbon nanotubes and the range of functionalities used for anchoring of the clusters, make determination of their oxidation state and structure difficult. An analogous model system, graphene, can be prepared and studied under UHV conditions with great control. We employ scanning tunneling microscopy (STM) to study chemical functionalization of supported graphene on Ru(0001) with atomic oxygen. On Ru(0001) graphene forms a defect-free moiré structure with a periodicity of 3 nm, offering variety of distinct, regularly-spaced adsorption sites. Three different regions can be distinguished in STM images: bright regions (C atop of Ru) with the largest distance to the underlying Ru metal, dark hcp regions where graphene is closest to the metal, and medium-bright fcc regions where graphene is slightly further away compared to the hcp regions. Interestingly, for temperatures above 114 K, atomic oxygen (AO) is preferentially observed within the medium-bright fcc regions but in a minority of cases also in the hcp regions. The onset of AO mobility is observed at 400 K, where AO is occasionally moving inside the fcc region, or away from the less-stable hcp region towards the bordering fcc region. At higher temperatures (450-500 K), a dramatic increase in AO diffusion is observed allowing for AO transport between neighboring fcc regions through the hcp region. Upon encounter, the AO groups form stable immobile dimers and large clusters. The high-resolution time-lapsed data is used to assign the AO adsorption configuration to the on-top bonded enolate groups rather than the expected bridge-bonded epoxys. Our ongoing effort focuses on quantifying the enolate diffusion barrier and understanding their interactions with adsorbates such as H_2O, CO, and CO_2. The high thermal stability of enolate groups, and their large periodic separation (~3 nm) makes functionalized graphene/Ru(0001) an ideal model system for model studies of monodispersed catalysts.

11:20am **SS+AS+HC-MoM10 Interaction of BaO with H_2O, CO_2 and NO_2 Studied with APXPS and NEXAFS***, **Osman Karslioglu**, I. Zegkinoglou, L. Trotochaud, H. Bluhm,* Lawrence Berkeley National Laboratory

Barium is a constituent of several technologically important materials such as NO_x storage and reduction (NSR) catalysts in automobiles, getters for UHV applications, perovskite catalysts for electrochemical reactions and high-temperature superconductors. Interaction of barium compounds with simple molecules such as H_2O, CO_2 and NO_2 is thus of practical importance. We studied the interaction of in-situ prepared BaO with H_2O, CO_2 and NO_2 as a function of temperature and pressure using ambient pressure X-ray photoelectron spectroscopy (APXPS) and near-edge X-ray absorption fine structure (NEXAFS). Using in-situ preparation proved essential for preparing clean BaO, as the compound is extremely reactive even with minute amounts of H_2O and CO_2. We report the first experimental O K-edge X-ray absorption spectrum of clean BaO, for which the published spectra in the literature are more consistent with $BaCO_3$.

Plasma Science and Technology
Room 104D - Session PS+AS+SS-MoA

Plasma Surface Interactions

Moderator: Richard van de Sanden, FOM Institute DIFFER, Netherlands

1:40pm **PS+AS+SS-MoA1 Atomic-scale Analyses of Plasma Etching for Unconventional Materials in Microelectronics*, Satoshi Hamaguchi,* *K. Karahashi,* Osaka University, Japan **INVITED**

As the sizes of semiconductor devices continue to diminish and are now approaching atomic scales, the downsizing of transistors following Moore's law is bound to end in the near future. However, the continuing market demand for higher performance and lower energy consumption of large-scale integrated (LSI) circuits has driven invention of new device technologies such as three-dimensional (3D) device structures and devices based on non-silicon materials. Manufacturing of these non-conventional devices also poses new challenges for processing technologies. For example, magnetic materials used in magnetoresistive random-access memories (MRAMs) cannot be etched efficiently by the existing reactive ion etching (RIE) technologies, which has so far limited the level of integration of MRAM devices. The modern near-atomic-scale devices also require atomic level precision in their manufacturing processes, which has also driven new technologies such as atomic layer deposition (ALD) and atomic layer etching (ALE). In this study, we shall review our recent work on analyses of etching selectivity and surface chemical reactions for magnetic materials [1,2] metal oxides[3,4], Si-based materials [4] as well as damage formation mechanisms [6,7] due to ion bombardment during RIE processes. In our analyses, we use multi-beam injection experiments [8] and molecular dynamics (MD) simulations to emulate elementary processes of plasma-surface interactions that take place in RIE processes.

References

[1] M. Satake, M. Yamada, H. Li, K. Karahashi, and S. Hamaguchi, J. Vac. Sci. Tech. B **33** (2015) 051810.

[2] H. Li, Y. Muraki, K. Karahashi, and S. Hamaguchi, J. Vac. Sci. Tech. A **33** (2015) 040602.

[3] H. Li, K. Karahashi, M. Fukasawa, K. Nagahata, T. Tatsumi, and S. Hamaguchi, J. Vac. Sci. Tech. A **33** (2015) 060606.

[4] H. Li, K. Karahashi, M. Fukasawa, K. Nagahata, T. Tatsumi, and S. Hamaguchi, Jpn. J. Appl. Phys. **55** (2016) 021202.

[5] K. Miyake, T. Ito, M. Isobe, K. Karahashi, M. Fukasawa, K. Nagahata, T. Tatsumi, and S. Hamaguchi, Jpn. J. App. Phys. **53** (2014) 03DD02.

[6] K. Mizotani, M. Isobe, and S. Hamaguchi, J. Vac. Sci. Tech. A **33** (2015) 021313.

[7] K. Mizotani, M. Isobe, M. Fukasawa, K. Nagahata, T. Tatsumi and S. Hamaguchi, J. Phys. D: Appl. Phys. **48** (2015) 152002.

[8] K. Karahashi and S. Hamaguchi, J. Phys. D: Appl. Phys. **47** (2014) 224008.

2:20pm **PS+AS+SS-MoA3 Plasma Wall Interactions: Y_2O_3 Wall Interaction in Cl_2 Plasma Etching of Si and NF_3 Plasma Cleaning*, Tianyu Ma,* *T. List, V.M. Donnelly,* University of Houston

The walls of a plasma etching chamber play a critical role in causing variability of processing metrics such as rate, profile shape and selectivity. Small changes in the nature of the chamber wall surfaces can affect radicals sticking coefficients, recombination probabilities, and other heterogeneous reactions that will cause changes in the number densities of species in the plasma, which in turn affects the process. Therefore, a stable chamber wall material is essential for plasma processes, and in particular plasma etching. Compared to traditional alumina and silica wall material, Y_2O_3 has high chemical stability and extending lifetime, making it one of the preferred wall materials in etching systems. Consequently, studies were performed in a chamber with Y_2O_3-coated walls to determine time-dependent variations in the number densities of species in inductively coupled Cl_2/Ar and NF_3/Ar plasmas. Si was etched in Cl_2 plasmas, after which, the wafer was removed and an NF_3 plasma was used to remove etching products that deposited on the walls. This etch-clean procedure was repeated many times, simulating an integrated circuit manufacturing etch process. Optical emission spectroscopy (OES) and Langmuir probe analysis were performed to characterize plasma. Y_2O_3-coated coupon pieces exposed to the plasma were examined by X-ray photoelectron spectroscopy (XPS). Number densities of Cl_2, Cl, O, and F were obtained with rare-gas actinometry during the entire etching and cleaning cycles. Emissions from Si, SiCl, $SiCl_2$, $SiCl_3$, SiF, and N_2 were also recorded. After exposure to the NF_3 plasma, Cl number densities are relatively low when no substrate bias is placed on the Si substrate. As soon as bias is initiated, Cl number density rises steeply at first and then slowly maximizes. This is attributed to then displacement of F on the walls with a $SiCl_x$ containing layer. Apparently Cl on its own cannot remove F efficiently, but the reaction of Si-containing etching products produces SiF surface species that desorb and are observed as transient SiF emission in the first moments of etching. Cl recombination on this surface is much lower than on the fluorinated Y_2O_3 surface. Once prepared by etching Si with bias, the Cl number density remains high if bias is extinguished and etching nearly stops. The higher recombination coefficient on fluorinated surfaces is attributed to the longer residence time of physisorbed Cl, caused by the attraction to positively charged Y sites that are created when Y forms mainly ionic bonds with F.

2:40pm **PS+AS+SS-MoA4 Novel atomic order CD Control Technology by Fusion of Quasi-ALE and ALD*, Yoshihide Kihara,* *T. Hisamatsu,* Tokyo Electron Miyagi Limited, Japan*; T. Oishi, S. Ogawa, H. Watanabe,* Tokyo Electron Miyagi Limited*; A. Tsuji, M. Honda,* Tokyo Electron Miyagi Limited, Japan

In the recent years continuous scaling has required the use of multiple mask patterning technologies such as double and quadruple patterning, and increasingly thin EUV mask films are being planned to be used in the near future. In the patterning process, the fabrication of multilayer films requires the precision of atomic layer level accuracy (within nm level). Some critical challenges that patterning schemes face includes thinning of mask materials, reduction of ARDE related CD-loading, and reduction of LER and LWR. This requires the realization of highly selective etch processes that can address the challenges without trade-offs in other process specifications.

One method to increase the mask selectivity to enable mask thinning, which is one of the major patterning issues, Si-ARC is etched in a depositing condition which protects the resist mask surface, utilizing the material difference between the mask material and the antireflective layer (Si-ARC). However, to enhance selectivity, extra amount of the deposition can be generated. The amount of deposition flux fluctuates depending on the pattern density, leading to CD loading. In order to solve the tradeoff between selectivity and loading, we have proposed a Quasi- Atomic Layer Etching (Quasi-ALE) which is a modification of ALE to employ thin-film adsorption and activation by low ion energy [1]. In this paper, Quasi-ALE is applied to Si-ARC etch step to address three challenges; high selectivity, pattern-independent CD-loading, and vertical etch profiles.

We have also proposed the combination of ALD with etch as CD-loading-free CD control technique [2]. By combining ALD and Quasi-ALE, excellent CD controllability was achieved to address the entire patterning process issues without tradeoffs. In the presentation, various merits of the Fusion Process, which is a combination of Quasi-ALE and ALD, in patterning process, will be introduced. Fusion Process has a significant potential to solve critical challenges in the patterning process of N7, N5 and beyond.

Reference

[1] A.Tsuji et al., AVS 62nd Int. Symp. (2015)

[2] T.Hisamatsu et al., AVS 62nd Int. Symp. (2015)

3:00pm **PS+AS+SS-MoA5 Development of a New Analysis Technique of Nanostructures Etched by Plasmas: Quasi In-Situ TEM EDX Characterization*, Matthieu Serege,* LTM, Univ. Grenoble Alpes, CEA-LETI*; G. Cunge,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; L. Vallier, E. Latu-Romain,* LTM, Univ. Grenoble Alpes, CEA-LETI*; O. Joubert,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

As the size of integrated circuit continues to shrink, plasma processes are more and more challenged and show limitations to etch nanometer size features in complex stacks of thin layers. The achievement of anisotropic etching relies on the formation of passivation layers on the sidewalls of the etched features which act like a protective film that prevents lateral etching by the plasma radicals. However, this layer also generate a slope in the etch profile and it's difficult to control the layer thickness. Another thin layer called "reactive layer" is also formed at the bottom of the feature where the energetic ion impact mix the material to be etched with the plasma radicals. Etch products are formed allowing a high etch rate of the silicon substrate. It starts to be realized that controlling the thickness of this reactive layer is the key to achieve very high selective processes. Indeed, accurate etch stop on an ultra-thin layer is only possible if the thickness of this stop layer is higher than the thickness of the reactive layer otherwise damages are created underneath the stop layer.

A better understanding of these layers chemical nature, thickness and deposition mechanism is mandatory, but the main problem is that the layers to be analyzed are chemically highly reactive because they contain large concentrations of halogens and they get immediately modified (oxidized) when exposed to ambient atmosphere.

In this work we develop an original, simple and extremely powerful approach to observe passivation layers quasi in-situ (i.e. without air exposure): After plasma etching, the wafer is transported *under vacuum* inside an adapted suitcase to a deposition chamber where it is encapsulated by a metallic layer (magnetron sputtering PVD). Then, the encapsulated features can be observed ex situ without chemical / thickness modification using FIB-SEM (specimen preparation) coupled with a TEM-EDX analysis: HRTEM observation provides an extremely precise measurement of the passivation layer and encapsulation morphology. In parallel, STEM-EDX is used to map the main atomic element in our specimen, supplying qualitative information on the layer chemical composition. STEM-EDX is also used in profile mode to give us more accurate quantitative analysis. We are able to estimate the (relative) quantitative atomic concentration along a line scan profile on the feature sidewalls.

The measurements relatively fast, provide accurate analysis at the nanoscale, and are highly promising to better understand plasma etching processes. Therefore, this technique will be very helpful to develop innovative processes controlled at the nanometer range.

3:20pm **PS+AS+SS-MoA6 Atomistic Simulations of He Plasma Modification of Si/SiN Thin-Films for Advanced Etch Processes***, **Vahagn Martirosyan,*** LTM, Univ. Grenoble Alpes, CEA-LETI, France*; E. Despiau-Pujo,* CNRS - LTM, France*; 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 (e.g. FDSOIs, FinFETs). 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 (H 2) 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 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-He and Si-N- He systems

and provide an overview of the reaction processes at the atomic scale. The objective is to understand

precisely the role of ion energy in the self-limited ion implantation, and to determine the relationship

between the flux/energy of plasma species (He +) bombarding the surface and its structural/chemical

modifications.

In this work, we investigate the interaction between helium plasma species (He+ ions) and

silicon/silicon nitride via MD simulations, by studying the influence of ion energy (5-100eV) and ion

dose on the substrate modification. For He/Si interactions, simulations show an initial He implantation

followed by the formation of a stable modified layer at steady state, composed of two parts: a Si-He

mixed amorphous layer and a thin sublayer, which is crystalline but enriched in helium. According to

our results, the higher is the ion energy, the more rapid is the contamination and the thicker is the

amorphous layer. Few or no Si sputtering is observed for energies lower than 100eV, confirming that

He plasmas can modify/weaken the material on a precise depth without etching it. Amorphisation of

the material leads to the rupture of crystalline Si-Si bonds and to the creation of a less dense modified

layer, facilitating its subsequent removal by wet or dry etching. Mechanisms of helium

retention/desorption, as well as comparisons between He/Si and He/SiN interactions, will be

discussed during the presentation.

References

1. N. Posseme, O. Pollet, S. Barnola, Applied Physics Letters 105, 051605 (2014)

4:20pm **PS+AS+SS-MoA9 Patterned Chromium Hard Mask Etching in a Two Reactant Gas for Bit Patterned Media Template Fabrication***, **Daniel Staaks**[*],* Molecular Foundry, Lawrence Berkeley National Lab*; X. Yang,* Seagate Technology*; S. Dallorto, S.D. Dhuey, S. Sassolini,* Molecular Foundry, Lawrence Berkeley National Lab*; K.Y. Lee,* Seagate Technology*; I.W. Rangelow,* Ilmenau University of Technology, Germany*; D.L. Olynick,* Molecular Foundry, Lawrence Berkeley National Lab

Plasma-based dry etching is one of the most important nanofabrication methods for transferring full-wafer patterns. As feature sizes approach the single digit nanometer regime, there is an urgent need to develop a comprehensive and detailed understanding of the associated etching mechanisms. Additionally, challenges in obtaining high anisotropy, high selectivity, and robust critical dimension control must be addressed.

Highly selective chromium etching masks are an area of particular interest. Chromium has a widespread utility in not only manufacturing photolithography masks, but also in fabricating high-resolution nanoimprint templates. For example, we use it as a highly selective hard mask when etching SiO2 to achieve Bit Patterned Media templates towards sub-5nm features ($7Tb/in^2$).

To date, there have been few investigations into patterned chromium films. The limited studies available involve micron-sized features and patterning by the erosion of polymer masks, which make extrapolation to the single-digit nano regime very difficult. In this work, we bridge the gap for nanoscale-patterned films. We etch a patterned 20nm layer of chromium in low pressure and low power Cl_2/O_2 plasmas. We investigate the profile evolution of features ranging from 15nm- to 200nm in pitch. Previous work in etching blanket chromium films revealed that chromium etch rate was influenced by substrate temperature and Cl_2/O_2 flow [1]. Here, we vary percent O_2 flow (1%, 50%, 87%) and temperature (-50°C, +20°C) to explore the effects on lateral etching mechanisms, etch lag, and anisotropy. Using a highly selective HSQ mask for etching the chromium allows us to better determine the involved etching mechanisms. High-resolution micrographs of thin film cross-sections show significantly enhanced anisotropy at low temperatures.

Additionally, the unique etching chemistry of chromium must be considered when evaluating the material as a mask. Most materials form multiple volatile binary compounds during the etching process. Chromium, on the other hand, forms a single ternary compound: chromyl chloride. This enables us to study the effect of two-reactant gas chemistry on the etched feature profile. Results indicate that gas phase transport and surface mass transport of oxygen and chlorine are influential to profile shapes. Moreover, the effective local oxygen concentration inside the trench is important, and surface-dominated reactions highly affect the profile. Chlorine rich and chlorine poor chemistries promote very different surface reactions.

[1] D. Staaks, et al., Low temperature dry etching of chromium towards control at sub-5 nm dimensions, Nanotechnology 2016, submitted manuscript

---

[*] **Coburn & Winters Student Award Finalist**

4:40pm **PS+AS+SS-MoA10 Alternative Solutions for Nanometric-Precision Etching: H2 Plasmas Modification of Si/ SiN Thin-Films***, **Emilie Despiau-Pujo**, V. Martirosyan, O. Joubert,* LTM - CNRS/Univ Grenoble Alpes/CEA, France

Consisting of several ultrathin layered materials, advanced transistors (FDSOI, FinFET) must be etched with a nanometric precision and nearly infinite selectivity to preserve the electronic properties of active layers (e.g. the silicon channel), a challenge which cannot be addressed by conventional CW plasma processes. To achieve uniform and damage-free etching of multi-layered transistors, an alternative etch approach has been recently proposed, consisting in two steps. In a first step, the film to be etched is modified in volume by exposition to a hydrogen or helium conventional CCP or ICP; in a second step, the modified layer is selectively removed by wet cleaning or exposure to gaseous reactants only. Such a two-steps process showed promising results for silicon nitride spacers etching [1]. To assist the development of this new technique, Molecular Dynamics (MD) simulations - coupled to experiments - are used to investigate the interactions between H2 plasmas and Si/SiN films. These atomic-scale simulations aim at better understanding the relationship between the flux/energy of plasma species (Hx+ ions, H radicals) bombarding the surface and its structural/chemical modifications.

Although one material of interest is silicon nitride, the study of Si-H systems constitutes a first step to understand the impact of ion energy (5-100 eV) and ion dose on the substrate modification and self-limited ion implantation. Simulations of cumulative Hx+ (x=1-3) ion bombardment show a rapid hydrogenation of Si followed by the formation of a stable modified layer at steady state. This modified layer is composed of a thick amorphous Si-H mixed layer and a thin sublayer, quasi-crystalline but enriched in hydrogen. As hydrogen is highly chemically reactive, ion implantation leads to the rupture of crystalline Si-Si bonds and to the creation of SiH, SiH2, SiH3 covalent bonds in the modified material. At the bottom of the modified layer, hydrogen tends to saturate the dangling bonds of the amorphous silicon and to create SiH3 bonds, thus fracturing the substrate into a modified hydrogenated layer weakly bound to the underlying crystalline material (Smartcut-like mechanism). The influence of ion dose, ion energy and ion type on the modified layer thickness (and thus on the subsequent etch precision) are discussed. Comparisons between pure ion implantation and exposition to various H2 plasma conditions (simulated by bombarding the Si/SiN substrates with both Hx+ ions and H radicals) are also presented. [1] N. Posseme, O. Pollet, S. Barnola, Applied Physics Letters 105, 051605 (2014)

5:00pm **PS+AS+SS-MoA11 Plasma Dynamics at the Surface Interface in Low Pressure Capacitively and Inductively Coupled Plasmas***, **Martin Blake**, D. O'Connell,* University of York, UK*; A.R. Gibson,* LPP, CNRS, Ecole Polytechnique, Université Paris-Saclay, France*; T. Gans,* University of York, UK

The plasma-surface interface in low temperature, low pressure plasmas used for industrial

wafer processing is difficult to characterise. However, understanding the plasma dynamics

at this interface is key for further optimisation of industrial plasma processes. Of particular

relevance are the densities of reactive species, such as atomic oxygen, in this region. In this

work a methodology has been developed based on newly augmented fast optical

techniques which can probe reactive species densities in the wafer region without the need

for expensive laser equipment. This technique, known as energy resolved actinometry

(ERA)[1], utilises phase resolved optical emission spectroscopy (PROES) measurements of the

direct and dissociative electron-impact excitation dynamics of three distinct emission lines,

750.4 nm (argon, added in small concentrations as a tracer gas) and 777.4 nm, 844.6 nm

(atomic oxygen). Through the ratio of the excitation functions and their energy dependence

we determine both the atomic oxygen density and the mean electron energy above the electrode surface.

In this work ERA has been applied to measure atomic oxygen densities and local mean

electron energies in a low pressure (1 – 100 Pa) oxygen plasma produced in a GEC reference

cell system [2], operated at 13.56 MHz in both capacitive and inductive modes at power

inputs ranging from 50 – 500 W. Additional characterisation of the plasma-surface interface

is carried out through the use of a retarding field energy analyser (RFEA) to measure the ion

energy distribution at the surface. The combination of both approaches allows for

information on the neutral and ion dynamics in the surface region, both of which are known

to be important for process outcomes.

A two-dimensional hybrid plasma simulation code is used to simulate the same conditions in

order to improve understanding of the experimental results.

Acknowledgements:

This work has been supported through the UK Engineering and Physical Sciences Research

Council (EPSRC) manufacturing grant EP/K018388/1 and the authors would also like to thank

Intel Ireland, Ltd. for financial support.

References:

[1] Greb, A., Niemi, K., O'Connell, D., Gans, T. 2014; Energy resolved actinometry for

simultaneous measurement of atomic oxygen densities and local mean electron energies in

radio-frequency driven plasmas, Appl. Phys. Lett. 105 234105

[2] P. J. Hargis Jr et al (1994); The Gaseous Electronics Conference radio-frequency reference

cell: A defined parallel-plate radio-frequency system for experimental and theoretical

studies of plasma-processing discharges, Rev. Sci. Instrum. 65, 140

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+2D+AS+NS+SS-MoA

Probing Topological States And Superconductivity

Moderators: An-Ping Li, Oak Ridge National Laboratory, Chuanxu Ma, Oak Ridge National Laboratory

1:40pm **SP+2D+AS+NS+SS-MoA1 Tuning Dirac States by Strain in Topological Insulators***, **Lian Li**,* University of Wisconsin-Milwaukee **INVITED**

Topological insulators (TIs) are distinguished by their metallic boundary states populated by massless Dirac fermions and bulk topological Z_2 index. Changes in the band topology induced by external variables such as strain, electrical field, and composition thus provide a means to tune the boundary states. As a large spin-orbit coupling is necessary to produce an inverted band gap, most TIs discovered to date are narrow gap semiconductors consisting of heavy elements. These materials typically exhibit layered crystal structure with anisotropic bonding characteristic: strong covalent bonding in-plane and weak van der Waals (vdW) bonding out-of-plane, which has been predicted to facilitate effective strain engineering of their bulk band topology.

In this talk, I will first give an overview of the opportunities and challenges in the epitaxial growth of layered TIs. Using the prototypical 3D TI Bi_2Se_3 as an example, I will show that the characteristic anisotropic bonding facilitates a spiral growth mode on virtually any substrates by molecular beam epitaxy. The coalescence of these spirals results in a high density of grain boundaries that consist of alternating edge dislocation pairs, leading to periodic in-plane stretching and compression. Using scanning tunneling spectroscopy, I will show that this local strain field strongly modifies the Dirac surface states, where in-plane compression expands the vdW gap and destroys the Dirac states.

Next, I will show our recent work on the strain engineering of Dirac edge states of epitaxial Bi bilayer films grown on three different substrates: the (111) surface of 3D TIs Bi_2Se_3, Sb_2Te_3, and Bi_2Te_3. Using scanning tunneling microscopy/spectroscopy, I will show that for moderately strained (<6%) single Bi bilayer on Sb_2Te_3 and Bi_2Te_3, edge states are observed; while on highly compressed single Bi bilayer on Bi_2Se_3 (>8%), edge states are suppressed. These findings, supported by density functional theory calculations, demonstrate the uniform control of edge states in 2D topological insulators by strain.

2:20pm **SP+2D+AS+NS+SS-MoA3 Detection of Current Induced Spin Polarization in Topological Insulators via Four-Probe Spectroscopy***, **Saban Hus**,* Oak Ridge National Laboratory*; Y. Chen,* Purdue University*; A.-P. Li,* Oak Ridge National Laboratory

Charge currents carried by the nontrivial surface states of topological insulators (TIs) exhibit a net spin polarization due to spin-momentum locking. Electrical detection of such a spin polarization is crucial for technological applications. However, in 3D TI materials the existence of a bulk conduction channel makes it difficult to quantify the density and the spin polarization of the current carried by the surface states. Here we report in-situ, spin sensitive four-probe spectroscopy measurements on Bi_2Te_2Se single crystals. A ferromagnetic probe detects the net spin accumulation on the surface states while a set of four-probe spectroscopy measurement is used for a quantitative separation of 2D and 3D conduction. We also examine the effect of surface doping by residual gas molecules on the current induced spin polarization. Even though, the additional carriers by dopants enhance the 2D conductance in TIs they reduce the net spin polarization of current carried by topological surface states.

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

2:40pm **SP+2D+AS+NS+SS-MoA4 Switching Handedness of Chiral Solitons Under Z_4 Topology***, **Tae-Hwan Kim**,* Pohang University of Science and Technology, Republic of Korea*; S. Cheon, H.W. Yeom,* Institute for Basic Science (IBS), Republic of Korea

Chirality is a ubiquitous and interesting property of asymmetry in many fields ranging from biology, chemistry to physics. Because of its topologically distinct nature, such chiral objects in condensed matter are often topologically excited states, which are protected by system's topology and can be used to carry information robustly against external perturbations. For instance, nanoscale magnetic skyrmions, spatially localized chiral spin texture with particle-like properties in ferromagnets, have been investigated intensively as topological information carriers for next generation spintronic devices. However, logic operations using topological excitations such as skyrmions are only conceptually proposed. On the other hand, chiral solitons are recently discovered as the topologically protected edge states of one-dimensional Z_4 topological insulators [1,2], which can be exploited as topological information carriers in electronic system. In this talk, I show experimentally and directly that switching between solitons with different chirality is possible by merging them with achiral solitons [3]. I will also show that this chiral switching corresponds to the realization of topological addition of the Z_4 topological number or chirality. With their distinct topologically protected chirality, chiral solitons could uniquely be applied for robust multilevel information storage and logic operation by storing, carrying, and switching three differently topological bits of information.

[1] T.-H. Kim and H. W. Yeom, Phys. Rev. Lett. **109**, 246802 (2012).

[2] S. Cheon, T.-H. Kim, S.-H. Lee, and H. W. Yeom, Science **350**, 182 (2015).

[3] T.-H. Kim, S. Cheon, and H. W. Yeom, submitted (2016).

3:00pm **SP+2D+AS+NS+SS-MoA5 Spectroscopic-imaging STM Studies on Dirac-Landau Levels in the Topological Surface State***, **Tetsuo Hanaguri**,* RIKEN Center for Emergent Matter Science, Japan **INVITED**

We show that spectroscopic-imaging scanning tunneling microscopy (SI-STM) is a powerful tool to investigate unique electronic features of massless Dirac electrons in a magnetic field.

In contrast to the conventional massive electron that is described by a single-component wave function, the massless counterpart demands the two-component wave function. In the case of the surface state of topological insulators, these two components are associated with the spin degrees of freedom, thereby governing the magnetic properties. Thus, it is highly desirable for spintronics applications to elucidate where and how the two-component nature emerges. We found that the two-component nature manifests itself in the internal structures of Landau orbits. We visualized the local density-of-states (LDOS) distributions associated with the Landau orbits in the topological surface state of Bi_2Se_3 using SI-STM. In the presence of the potential variation, Landau orbits drift along the equipotential lines, forming ring-like patterns in the LDOS images. The observed internal structures of the rings are qualitatively different from those of conventional massive electrons but are well reproduced by the calculation based on a two-component model Dirac Hamiltonian. Our model further predicts non-trivial energy-dependent spin-magnetization textures around the potential minimum. This is originated from the interplay between the two components and may provide a clue to manipulate spins in the topological surface state.

In addition to the Landau orbits, we succeeded in observing the Zeeman shift of the lowest Landau level from which precise *g* factor of the massless Dirac electron can be estimated. We performed experiments on two topological insulators, Bi_2Se_3 and Sb_2Te_2Se, and determined the surface *g* factors of them to be 18 and -6, respectively. Such remarkable material dependence suggests that the Zeeman effect is tunable by controlling the chemical composition, providing a new knob in manipulating the spins in the topological surface state.

4:00pm **SP+2D+AS+NS+SS-MoA8 The Rashba and Quantum Size Effects in Ultrathin Bi films***, **Toru Hirahara**,* Tokyo Institue of Technology, Japan **INVITED**

Precise characterization of physical properties in nanometer-scale materials is interesting not only in terms of low-dimensional physics but also in application to devices. Due to the reduced dimensionality and symmetry, these systems possess various interesting properties that cannot be found in the bulk. In this presentation, focusing on epitaxial ultrathin bismuth films formed on a silicon substrate, we introduce an intriguing interplay of the quantum size and Rashba effects in reciprocal space. Utilizing spin- and angle-resolved photoemission spectroscopy, we observed clear Rashba-split nature of the surface-state bands in these Bi films. However, the band dispersion did not follow the simple Rashba picture and the spin-splitting was lost where they overlapped with the bulk projection. From first-principles calculations, this was explained as a change in the nature of the band-splitting into an even-odd splitting induced by the quantum size effect [1]. Furthermore, we show that the interplay of the quantum size effect and the presence of the surface state induces a complicated change in the Fermi level position of the bulk states in bismuth, which is critical in discussing the surface-state contribution in the film properties [2,3].

[1] T. Hirahara, Journal of Electron Spectroscopy and Related Phenomena **201**, 98 (2015).

[2] T. Hirahara, T. Shirai, T. Hajiri, M. Matsunami, K. Tanaka, S. Kimura, S. Hasegawa, and K. Kobayashi, Physical Review Letters **115**, 106803 (2015).

[3] M. Aitani, T. Hirahara, S. Ichinokura, M. Hanaduka, D. Shin, and S. Hasegawa, Physical Review Letters **113**, 206802 (2014).

4:40pm **SP+2D+AS+NS+SS-MoA10 Understanding the Microscopic Effects of Annealing in $Ba(Fe_{1-x}Co_x)_2As_2$ Superconductor***, **Qiang Zou**, Z. Wu, Q. Zheng, S. Rajputł, D.S. Parker, A.S. Sefat, Z. Gai,* Oak Ridge National Laboratory

By hole or electron doping of the parent iron-based $BaFe_2As_2$ compound, the high-transition temperature superconductivity emerges from the suppression of the antiferromagnetic order. [1] It was widely reported that thermal-annealing significantly improves some superconducting characteristics in $Ba(Fe_{1-x}Co_x)_2As_2$, including T_c [2] The microscopic origin of such effect is still an open question. To make a connection between the global and the microscopic behavior of the materials, we did a comparison measurement on the pair of well-characterized x, we call ' as-grown' vs 'annealed' $Ba(Fe_{1-x}Co_x)_2As_2$ crystals, and using low temperature scanning tunneling microscopy and spectroscopy (STM/S). The superconducting gap maps deducted from the dI/dV maps were compared. The gap width distribution of the as-grown sample are obviously narrower than that of the annealed one. The coherent peak position also shifted to higher value for the annealed sample. The corresponding reduced-gaps of $2\Delta/k_bT_{c1}$ are about 2.3 and 5.4 for the as-grown and annealed crystals, respectively. The difference of the reduced-gaps indicates that the pairing strength of the annealed crystal is stronger than the as-grown one.

This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division . A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Reference

1. Stewart, G. R. (2011). "Superconductivity in iron compounds", *Reviews of Modern Physics*, *83*(4), 1589.

2. Gofryk, K., et al. "Effect of annealing on the specific heat of $Ba(Fe_{1-x}Co_x)_2As_2$" *Physical Review B, 83(6), 064513*

5:00pm **SP+2D+AS+NS+SS-MoA11 Annealing Effect on the Properties of Superconducting Parent $BaFe_2As_2$ Crystal***, **Shivani Rajput**, Q. Zou, A.S. Sefat, Z. Gai,* Oak Ridge National Laboratory

Understanding of electronic interactions in a parent phase of a superconducting crystal is crucial in determining the mechanism behind high Tc superconductivity. Bulk measurements show that annealing of parent $BaFe_2As_2$ crystal at 700 ^{0}C for 30 days causes a 5 K shift in magnetic transition temperature (T_N) compared to as grown crystal. To understand the effect of annealing and details of magnetic phase transition, we investigate as-grown and annealed $BaFe_2As_2$ crystals at atomic scale using a variable temperature scanning tunneling microscopy/ spectroscopy at various temperature points across T_N. Tunneling spectroscopy exhibit a ~ 0.53 eV gap type feature above T_N, while V-shape dI/dV spectra below T_N. The dI/dV mapping measurements show that as-grown $BaFe_2As_2$ crystals are electronically inhomogeneous, and averaging the differential conductance spectra over a large area does not truly represent the electronic properties of the sample at local scale, whereas annealed sample is comparatively electronically homogeneous.

This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Surface Science
Room 104E - Session SS+AS+HC-MoA
Metals, Alloys, and Oxides: Reactivity and Catalysis

Moderator: David Mullins, Oak Ridge National Laboratory

1:40pm **SS+AS+HC-MoA1 Scanning Tunneling Microscopy Studies of Hydrogen adsorption on the $RuO_2(110)$ Surface***, **Arjun Dahal**, R. Mu, Z. Dohnálek, I. Lyubinetsky,* Pacific Northwest National Laboratory

Understanding of hydrogen/oxide interactions is important for a variety of fundamental and applied processes. By using high resolution scanning tunneling microscopy (STM), we probed the adsorption of H_2 (or D_2) on model catalyst $RuO_2(110)$ surface, which has wide range of applications in heterogeneous catalysis, hydrogen storage, and many other energy related areas. Well-defined $RuO_2(110)$ surface exposes alternating rows of bridge-bonded oxygen atoms (O_b) and five-fold-coordinated Ru atoms (Ru_{cus}). STM data indicate that hydrogen molecule dissociates even at 5 K, whereas one hydrogen adatom adsorbs on top of the Ru_{cus} site (producing a hydrate, H-Ru_{cus}, species) and the second on top of the adjacent O_b site (forming a bridging hydroxyl, H-O_b, species), generating an H-Ru_{cus}/H-O_b pair. For the low hydrogen coverage, the dissociated H-Ru_{cus}/H-O_b pairs adsorb on every alternate Ru_{cus}/O_b sites adopting a (2×1) registration. When $RuO_2(110)$ surface adopts a such registration of the H-Ru_{cus}/H-O_b pairs locally, hydrogen starts to adsorb molecularly on top of the Ru_{cus} sites in between the adjacent dissociated hydrogen-pairs. With further increase of hydrogen coverage, linear arrays of H_2 molecules are formed along Ru_{cus} rows. The saturation coverage of the hydrogen on the $RuO_2(110)$ surface is observed to be ~0.75 ML, where 1 ML is designated as the Ru_{cus} site density on the stoichiometric $RuO_2(110)$ surface ($5.06x10^{14}$ cm^{-2}). Upon annealing the hydrogen-covered $RuO_2(110)$ surface, H_2 molecules from the linear array desorb around 110 K. On the other hand, the H-R_{cus} species of H-R_{cus}/H-O_b pair transforms (via a proton transfer) into another H-O_b group, across-row from original H-O_b group, producing crosswise H-O_b/H-O_b pair at temperatures above ~250 K.

2:00pm **SS+AS+HC-MoA2 Metal Vapor Adsorption Calorimetry on Layered Ca Niobate Nanosheets: Energetics and Adsorbate Structure***, **Wei Zhang**, J. Lownsbury,* University of Washington*; R. Uppuluri, T.E. Mallouk,* The Pennsylvania State University*; C.T. Campbell,* University of Washington

The metal/oxide interface is essential to many current and prospective technologies, including oxide-supported metal catalysts, fuel cells, photocatalysis, and nanoscale electronic contacts, so understanding the strength of metal – oxide bonding at such interfaces is of great interest. These strengths have been measured on single crystal oxide surfaces by single crystal adsorption calorimetry (SCAC) of metal atom adsorption in ultrahigh vacuum (UHV)[1] and on niobate and tantalate nanosheets by solution-based isothermal titration calorimetry during the deposition of transition metal oxide (or hydroxide) nanoparticles from their aqueous salt solutions[2,3]. These niobate nanosheets are very interesting since they are highly ordered and essentially like single crystal surfaces in that the ratio of terrace sites to defect and edge sites is huge. Furthermore, when used as supports for transition metal oxide nanoparticles, they have been shown to display unusual stability against sintering.[2,3] Here, we directly measure the adsorption energies of metal vapor on such niobate nanosheets using SCAC in UHV. Specifically, we study the adsorption of Ca and Ag vapor onto calcium niobate films that are 4 nanosheets thick (~4 nm total). Calcium atoms show a sticking probability near unity and an initial heat of adsorption of ~660 kJ/mol, much higher than the heat of bulk Ca(s) sublimation (178 kJ/mol). Low-energy ion scattering spectroscopy (LEIS), which is element-specific and probes only the topmost atomic layer, is used to investigate the resulting metal particle/film morphology. The possible chemical reactions between the metal vapor and the calcium niobate during adsorption are elucidated using X-ray photoelectron spectroscopy (XPS).

[1] Campbell, C. T.; Sellers, J. R. V. *Faraday Discussions* **2013**, *162*, 9.

[2] Strayer, M. E.; Binz, J. M.; Tanase, M.; Shahri, S. M. K.; Sharma, R.; Rioux, R. M.; Mallouk, T. E. *J. Am. Chem. Soc.* **2014**, *136*, 5687.

[3] Strayer, M. E.; Senftle, T. P.; Winterstein, J. P.; Vargas-Barbosa, N. M.; Sharma,R.; Rioux, R. M.; Janik, M. J.; Mallouk, T. E. *J. Am. Chem. Soc.* **2015**, *137*, 16216.

2:20pm **SS+AS+HC-MoA3 Structure and Reactivity of Model Iron Oxide Surfaces***, **Gareth Parkinson**,* TU Wien, Austria **INVITED**

Iron oxides are abundant in nature and extensively utilized in modern technologies including heterogeneous catalysis [1]. Magnetite (Fe_3O_4), for example, is the active phase of the industrial water-gas shift catalyst, while hematite (Fe_2O_3) is used as the photoanode for photoelectrochemical water splitting. In this talk I will discuss our recent investigations of the $Fe_3O_4(100)$ and $Fe_2O_3(1\text{-}102)$ surfaces using a combined experiment/theory approach. The $Fe_3O_4(100)$ surface forms a reconstruction based on an ordered array of subsurface cation vacancies that contains exclusively Fe^{3+}, and is relatively inert [2]. Although formic acid adsorbs dissociatively at regular lattice sites [3], methanol adsorption is restricted to defects containing Fe^{2+} [4]. The bulk of the talk will focus on a detailed study of water adsorption on $Fe_3O_4(100)$ by TPD, STM, XPS, UPS, DFT+U and molecular dynamics calculations. In the remaining time I will demonstrate that a bulk terminated $Fe_2O_3(1\text{-}102)$ surface can be prepared by annealing in 10^{-6} mbar O_2, and a reduced (2x1) surface forms rapidly when heating in UHV. The structure of the (2x1) reconstruction and its reactivity toward water will be discussed.

[1] G.S. Parkinson, Iron oxide surfaces, Surface Science Reports (2016), http://dx.doi.org/10.1016/j.surfrep.2016.02.001

[2] R. Bliem, E. McDermott, P. Ferstl, M. Setvin, O. Gamba, J. Pavelec, M.A. Schneider, M. Schmid, U. Diebold, P. Blaha, L. Hammer, G.S. Parkinson, Subsurface Cation Vacancy Stabilization of the Magnetite (001) Surface, Science 346 (2014) 1215-1218.

[3] O. Gamba, H. Noei, J. Pavelec, R. Bliem, M. Schmid, U. Diebold, A. Stierle, G.S. Parkinson, Adsorption of Formic Acid on the $Fe_3O_4(001)$ Surface, The Journal of Physical Chemistry C 119 (2015) 20459-20465.

[4] O. Gamba, J. Hulva, J. Pavelec, R. Bliem, M. Schmid, U. Diebold, G.S. Parkinson, The role of surface defects in the adsorption of methanol on $Fe_3O_4(001)$, Topics in Catalysis submitted (2016).

3:00pm **SS+AS+HC-MoA5 Structure and Ethanol Reactivity of Ti-modified $CeO_x(111)$ Mixed Oxide Surfaces***, E.W. Peterson, **Jing Zhou**,* University of Wyoming

Ceria has been widely studied as an oxidation-reduction catalyst due to its unique redox properties and oxygen storage capacity. There has been an interest to incorporate additional metal dopants such as Ti into ceria to potentially enhance the thermal stability as well as improve the redox properties for practical applications in catalysis. This paper focuses on the fundamental mechanistic understanding of the effect of Ti dopant on the structure and reactivity of ceria using scanning tunneling microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy and temperature programmed desorption techniques. In the study, submonolayer coverage of Ti was deposited on well-ordered CeO$_x$(111) (1.5<x<2) thin films at room temperature. XPS studies show that Ti is oxidized to Ti^{4+} at the cost of Ce^{4+} reduction. Observation of CO IR band at 2173 cm^{-1} further confirms the presence of titania on the ceria surface. At 300 K, small atomic-like features of Ti-O-Ce linkages are present on ceria, which can coalesce into chain structures after heating to 700 K. Upon ethanol adsorption at 300 K, ethoxy was the surface intermediate observed on both oxidized and partially reduced ceria surface. With heating, it can go through the dehydration or dehydrogenation process to form acetaldehyde, ethylene, water and hydrogen products. Our studies have demonstrated that addition of Ti in ceria can affect the dehydration and dehydrogenation selectivity. Furthermore, the nature of ceria supports associated with oxygen vacancies and Ti dopants can have a promotional effect in the stability of deposited metal nanoparticles, such as Ni, and the chemical behavior toward the adsorption and reaction of ethanol. The research is sponsored by the National Science Foundation Career Grant (Award Number: CHE1151846) and the Wyoming NASA EPSCoR (NASA Grant: NNX13AB13A).

3:20pm **SS+AS+HC-MoA6 New Insights into the Coverage-Dependent Structure and Desorption Kinetics of CO on Palladium(111)**, ***Pan Xu,*** Stony Brook University; *S.-Y. Hong,* Brookhaven National Laboratory; *S. Liu,* Stony Brook University; *N.R. Camillone, M.G. White, N. Camillone,* Brookhaven National Laboratory

Carbon monoxide adlayers on palladium surfaces have, since the early days of ultrahigh-vacuum surface science, served as model systems for the study of molecule–surface interactions, structure and dynamics. As part of a recent study of the dynamics of ultrafast molecule–surface energy transfer we have revisited the CO/Pd(111) system and found that it continues to teach us about the complexities of molecule–surface interactions. Specifically, it has long been known that CO adlayers assume a wide range of ordered structures on Pd(111) at low temperature (~80 K). In fact, between the (√3×√3)R30° 0.33-ML and (2×2) 0.75-ML (saturation) structures, at least 17 well-ordered structures have been identified. Until now, however, a comprehensive correlation between these structures and the thermal desorption kinetics has not been reported. In this talk we detail a systematic investigation that correlates individual temperature-programmed desorption (TPD) features with specific adlayer structural phase transitions. We report that in addition to the spectrum of previously-observed structures we have observed for the first time, to the best of our knowledge, a well-developed, ordered domain-boundary structure at a coverage just below saturation. We have assigned this structure as a c(16×2) adlayer comprised of stripes with local (2×2) structure and used density functional theory to investigate the adsorption site preferences within the adlayer. We show how our results, in combination with existing data, can be interpreted in terms of a compromise between the energy minimization that accompanies binding at high-symmetry sites and lateral repulsive interactions. Furthermore, we describe how quantifying the coverage using the integrated desorption yield areas is problematic due to difficulties in growing a fully-saturated adlayer. We attribute these difficulties to a kinetic limitation of the structural phase transitions at high coverage, and show that this limitation is easily addressed by preparing the adlayer at a somewhat elevated temperature. We also detail use of the inversion-optimization method to extract the coverage dependence of the desorption activation energy from the TPD measurements. We compare the resultant simulated TPD line shapes with those derived using the "leading-edge" analysis method.

4:00pm **SS+AS+HC-MoA8 Combined Experimental and Computational Study of Water on Fe$_3$O$_4$ (001)**, ***Jan Hulva,*** Vienna University of Technology, Austria; *M. Meier,* Universität Wien, Austria; *J. Pavelec, S. Maaß, R. Bliem, M. Schmid, U. Diebold,* Vienna University of Technology, Austria; *C. Franchini,* Universität Wien, Austria; *G.S. Parkinson,* Vienna University of Technology, Austria

The interaction of water with metal-oxide surfaces is an important topic for a wide range of technological and environmental applications. This is particularly true for the iron oxides because of their abundance in nature and their use in chemical processes where water is involved e.g. the water-gas shift reaction [1]. Recent studies of water on iron oxide surfaces have found significant complexity, with evidence for pressure dependent adsorption, mixed-mode adsorption and coverage dependent hydrogen bonding [2-4]. Here we use a multi-technique experimental approach combined with ab-initio calculations including molecular dynamics to disentangle the coverage and temperature dependent behavior of water on the reconstructed Fe3O4(001)-(√2x√2)R45° surface [5]. Temperature programmed desorption shows that the first monolayer of water desorbs from the surface in four distinct peaks between 150 K and 250 K. Based on XPS, STM images and ab-initio calculations, we conclude that the first three peaks originate from molecular water desorbing from a coverage-dependent hydrogen-bonded network, while the last peak results from recombinative desorption from a partially dissociated water trimer species. Two additional desorption states at 340 K and 520 K are ascribed to desorption from surface defects and recombinative desorption of the surface surface hydroxyl groups, respectively.

[1] Parkinson, G.S., " Iron oxide surfaces", *Surface Science Reports* (2016)

[2] Dementyev, P., et al. "Water Interaction with Iron Oxides." *Angew.Chem. Int. Ed.* 54 (2015): 13942

[3] Mulakaluri, N., et al. "Partial dissociation of water on Fe$_3$O$_4$ (001): Adsorbate induced charge and orbital order." *Phys. Rev. Lett.* 103 (2009): 176102.

[4] Kendelewicz, T., et al. "X-ray photoemission and density functional theory study of the interaction of water vapor with the Fe$_3$O$_4$ (001) surface at near-ambient conditions." *J. Phys. ChemC* 117 (2013): 2719-2733.

[5] Bliem, R., et al. "Subsurface cation vacancy stabilization of the magnetite (001) surface." *Science* 346 (2014): 1215-1218.

4:20pm **SS+AS+HC-MoA9 Water Desorption from Sulfur-Doped Oxide Thin Films on W (100)**, ***Anthony Babore,*** *J.C. Hemminger,* University of California Irvine

Recent first principle calculations by Pacchioni and coworkers[1] suggest that sulfur dopants incorporated into the WO_{3-} lattice could favorably shift the band gap for enhanced visible light absorption. The present study aims to gain fundamental insight into the reactivity of a simple sulfur doped tungsten oxide system by using temperature programmed desorption (TPD) and water (D$_2$O) as a probe molecule. Furthermore, water desorption spectra were also obtained for pure oxide and pure sulfide films on W (100) for comparison. Auger electron spectroscopy (AES) was used to confirm the presence and relative amounts of sulfur and oxygen on the surface. TPD was then used to monitor the m/z 20, 19, and 18 signal intensity as a function of the temperature. To quantify the reactivity of water on the surface, activation energies of desorption were obtained. The results indicate distinct differences in the desorption spectra and desorption energies that exemplify the reactivity of each of the surfaces.

1. Wang F, Di Valentin C, Pacchioni G (2012) J Phys Chem C 116:8901–8909

4:40pm **SS+AS+HC-MoA10 Adsorption and Decomposition of Dimethyl Methylphosphonate on Metal Oxide Surfaces Under Atmospheric Conditions**, ***Ashley Head,*** *L. Trotochaud,* Lawrence Berkeley National Laboratory (LBNL); *R. Tsyshevsky,* University of Maryland College Park; *O. Karslioglu,* Lawrence Berkeley National Laboratory (LBNL); *M.M. Kuklja,* University of Maryland College Park; *H. Bluhm,* Lawrence Berkeley National Laboratory (LBNL)

Organophosphonates are used as corrosion inhibitors, pesticides, insecticides, and chemical warfare agents. This class of molecules has a range of acute toxicity, so dimethyl methylphosphonate is commonly used as a proxy for more toxic molecules. Metal oxides are used in applications for binding and decomposing organophosphonates despite little understanding of the chemistry and reactivity, especially in the presence of atmospheric molecules. With the ability to collect photoemission spectra at pressures up to about 25 Torr, ambient pressure XPS is well-suited to investigate the adsorption of DMMP in the presence of other molecules that have relevance to applications. Using MoO$_x$ and CuO$_x$ foils as model systems for chemical filtration materials, we have studied the adsorption and decomposition behavior of DMMP and how this behavior changes in the presence of atmospherically relevant molecules, including water, hydrocarbons, and NO$_x$. The effect of the small molecules on the substrate and the subsequent effects on DMMP binding, coverage, and decomposition will be discussed. APXPS results are interpreted with the aid of density functional theory calculations, which model DMMP adsorption, decomposition products, and reaction energies.

5:00pm **SS+AS+HC-MoA11 Oxygen Chemisorption and Thermal Oxidation of TiAlN High Power Pulsed Magnetron Sputtering Hard Coatings**, ***Martin Wiesing,*** *T. de los Arcos, G. Grundmeier,* University of Paderborn, Germany

The thermal oxidation of Ti$_{0.5}$Al$_{0.5}$N hard coatings as deposited by High Power Pulsed Magnetron Sputtering was investigated at reduced oxygen partial pressures of 10^{-6} and 10^{-2} Pa in a temperature range from 298 to 800 K. Quasi in-situ X-ray Photoelectron Spectroscopy and Low Energy Ion Scattering studies revealed oxygen to bind selectively to Ti-sites on the surface [1] and oxygen migration into the near-surface region. Three dimensional oxidation leads to the formation of a double layered surface oxide including a TiAl(O,N) growth region [2] terminated with a Ti^{IV} containing surface oxide [3]. Based on Wagner plot analysis, the surface oxide layer formed at 800 K can be described by a mixed $Ti^{IV}Al^{III}O_x$ phase while a separated $(Ti^{IV}O_2)(Al^{III}{}_2O_3)$ phase preferentially forms at 298 K. Complementary Ultraviolet Photoelectron Spectroscopy revealed a high degree of nitrogen doping in both cases.

The results are of importance for the design of multi-layered nitridic hard coatings and for a thorough understanding of the high-temperature oxidation resistance of such coatings.

Acknowledgement: The authors gratefully acknowledge the German Research Foundation (DFG) for financial support (SFB–TR 87). We thank Prof. Dr. J. Schneider and Holger Rueß for providing the coated specimen.

References:

[1] C. Kunze, D. Music, M. to Baben, J.M. Schneider, G. Grundmeier, Temporal evolution of oxygen chemisorption on TiAlN, Appl. Surf. Sci. 290 (2014) 504–508. doi:10.1016/j.apsusc.2013.11.091.

[2] S. Hofmann, Formation and diffusion properties of oxide films on metals and on nitride coatings studied with Auger electron spectroscopy and X-ray photoelectron spectroscopy, Thin Solid Films. 193–194, Part 2 (1990) 648–664. doi:10.1016/0040-6090(90)90216-Z.

[3] C. Gnoth, C. Kunze, M. Hans, M. to Baben, J. Emmerlich, J.M. Schneider, G. Grundmeier, Surface chemistry of TiAlN and TiAlNO coatings deposited by means of high power pulsed magnetron sputtering, J. Phys. Appl. Phys. 46 (2013) 084003. doi:10.1088/0022-3727/46/8/084003.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-TuM

Probing Chemical Reactions at the Nanoscale

Moderator: Tae-Hwan Kim, Pohang University of Science and Technology

8:00am **SP+AS+MI+NS+SS-TuM1 *In Situ* Probing of Oxygen Vacancy Diffusion Across Multilayer Oxide Heterostructures***, J. Zhu,* University of Massachusetts - Amherst*; J.-W. Lee, H. Lee,* University of Wisconsin - Madison*; R. DeSouza,* RWTH Aachen University, Germany*; C.-B. Eom,* University of Wisconsin - Madison*; **Stephen Nonnenmann**,* University of Massachusetts - Amherst

Complex oxide heterostructures display an extraordinary array of exotic collective and correlated physical phenomena that result from exploiting the strong interplay between structural and electronic degrees of freedom. Oxygen vacancies often facilitate or govern the interfacial phenomenon observed at or across well-defined discrete interfaces, ranging from domain wall pinning within ferroic systems to electron donors in conducting systems. Realization of multifunctionality within oxide heterostructures therefore necessitates a direct, proper understanding of the interrelationship exhibited by concomitant, defect-mediated transport mechanisms with adequate spatial resolution. Here we utilize a modified, *in situ* scanning probe technique to measure the surface potential across a multi-layered yttria-stabilized zirconia / strontium titanate (YSZ/STO) heterostructured film at 500 °C. Subsequent application of a classic semiconductor dopant formalism to the work function profile derived from the surface potential enables mapping of the oxygen vacancy distribution within STO with a resolution < 100 nm. The results presented herein demonstrate the promise of *in situ* scanning surface potential microscopy (SSPM) to investigate complex oxide interfacial systems multilayers that exhibit vacancy-dominated properties, under extreme environmental perturbation, on a highly localized scale.

8:20am **SP+AS+MI+NS+SS-TuM2 Study of Surface Chemistry on Various Noble Metal Surfaces by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy***, **Naihao Chiang**,* Northwestern University*; D. Chulhai,* Pennsylvania State University*; G. Goubert, L. Madison, X. Chen, E. Pozzi, M.C. Hersam, T. Seideman,* Northwestern University*; N. Jiang,* University of Illinois at Chicago*; L. Jensen,* Pennsylvania State University*; G. Schatz, R.P. Van Duyne,* Northwestern University

During the last few years, there has been an explosion of interest and activity in the field of nanoscale vibrational spectroscopy. Tip-enhanced Raman spectroscopy (TERS) combines the ability of scanning tunneling microscopy (STM) to resolve atomic scale surface features with the single molecule chemical sensitivity of surface-enhanced Raman spectroscopy (SERS). The goal is to understand and manipulate chemistry on the nanometer length scale using the properties of the collective electronic excitations in noble metal nanostructures, known as localized surface plasmon resonance (LSPR).

Two recent advances in ultrahigh vacuum (UHV) TERS which illustrate the power of this nanoscale vibrational spectroscopy will be presented. First, our current understanding of the adsorbate-surface and adsorbate-plasmon interactions involved in the UHV-TERS of the N-N'-bis(2,6-diisopropylphenyl)-perylene-3,4,9,10-bis(dicarboximide) (PDI) on various single crystal surfaces (Ag(111), Ag(100), Cu(111), and Au(111)) which probed by a Ag tip will be discussed. This study demonstrates that TERS is a substrate general technique. Additionally, the LSPR of the Ag tip-Ag sample junction is as broad as a Ag nanoparticle dimer system. Therefore, TERS on Ag tip-Ag sample systems is also excitation general.

Second, new insights into the nature of a conformational dynamics involved at room temperature will be described. We have interrogated the conformational change of *meso*-tetrakis-(3,5-di-tertiarybutylphenyl)-porphyrin (H_2TBPP) on a Cu(111) surface between two stable conformations. At room temperature, the barrier between the porphyrin ring buckling up/down conformations of the H_2TBPP-Cu(111) system is easily overcome, and our group has achieved unprecedented sub-nm resolution by simultaneous UHV-TERS and STM analysis. This topic illuminates that TERS can unambiguously distinguish the conformational differences between neighboring molecules with single molecule resolution. Furthermore, the sub-nm resolution led to the direct observation of single molecule transitions between states from one scan to the next.

8:40am **SP+AS+MI+NS+SS-TuM3 Exploring Surface-assisted Reactions Toward Functional Carbon Nanostructures***, **Xiaohui Qiu**,* National Center for Nanoscience and Technology, China **INVITED**

Understanding the dehydrogenation and dehalogenation reactions of molecular entities on surface is essential for the controlled synthesis of carbon-based nanostructures. Delicately designed precursor molecules exploit the potential of selective activation of functional groups and templating effect of substrates and promise the fabrication of nanoscale building blocks with desired geometries. Here we employed a combination of scanning tunneling microscopy, atomic force microscopy, and theoretical calculation to elucidate self-assembling of halogen-containing molecules on metal surfaces. Metallo-supramolecular assemblies are constructed via coordination bonding between metal atoms and halogen ligands. The spontaneously formed molecular scaffolds are further explored to program the structure and chemical composition of hybrid carbon architecture. We reveal the hierarchic reaction pathway of a few aromatic derivatives in an effort toward realizing carbon-based nanostructures with controllable electronic, optical and magnetic properties.

9:20am **SP+AS+MI+NS+SS-TuM5 Landscapes in Conversion of Quasi-Free-Standing Polymer Chains to Graphene Nanoribbons***, **Chuanxu Ma**,* Oak Ridge National Laboratory*; Z. Xiao,* North Carolina State University*; L. Liang,* Oak Ridge National Laboratory*; W. Lu, J. Bernholc,* North Carolina State University*; K. Hong, B.G. Sumpter, A.-P. Li,* Oak Ridge National Laboratory

Although the cyclodehydrogenation is well known as a key step in the bottom-up preparation of graphene nanoribbons (GNRs), the mechanism is still unclear. To understand and control the cyclodehydrogenation can help to create novel intraribbon heterojunctions of GNR-based structures. Here, we demonstrate the conversion of quasi-free-standing polymer chains to GNRs induced by thermal annealing and manipulations with a scanning tunneling microscope tip. Combined with the density functional theory calculations, a domino-like fashion and the hole-involved cyclodehydrogenation are proposed for the thermal annealing and tip-induced conversion of polymer chains to GNRs, respectively. Our results provide the first direct experimental evidence that the catalytic effect of the Au substrate is critical to the thermal-induced cyclodehydrogenation in forming bottom-up GNRs. Strongly localized density of states in the short GNR segment of the polymer–GNR herterojunction is observed. The significant confinement of the charge carriers is attributed to the big bandgap difference between the two segments of the heterojunction. Our findings might pave new ways to form GNR-based intraribbon heterojunctions by controlling the cyclodehydrogenation during bottom-up preparation, and shed light to the potential applications of the polymer–GNR herterojunctions.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility, and partially supported by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the US DOE.

11:00am **SP+AS+MI+NS+SS-TuM10 Imaging Single Molecule Chemistry***, **Wilson Ho**,* University of California Irvine **INVITED**

Single molecule chemistry can now be probed at unprecedented spatial resolution with a low temperature scanning tunneling microscope (STM) in ultrahigh vacuum. Advances in this field have provided new measurements and insights into the structure and function of molecules through real space imaging and high resolution vibrational spectroscopy. The combination of the STM with optical spectroscopy and femtosecond lasers has added a new dimension of time to space and enabled the probing of single molecule dynamics in light-matter interaction with better than 0.1 nm resolution. The ability to visualize single molecule chemistry has reinvigorated the study of molecules and their transformations on solid surfaces. Much of the scientific advancement and understanding in surface chemistry have derived from the well-defined conditions that have long been championed by surface science in providing unambiguous results that are appealing to the theoretical and experimental communities. Imaging single molecule chemistry has a broader impact on general chemistry due principally to direct visualization of molecules and their inner machinery at the limit of space and time.

11:40am **SP+AS+MI+NS+SS-TuM12 Atomic Force Microscopy: A Tool for Chemical Analysis of Surfaces and Molecules on Atomic Scale***, **Pavel Jelinek**,* Institute of Physics of the AS CR, Czech Republic **INVITED**

Atomic resolution and manipulation is routinely achieved by both scanning tunneling microscopy (STM) and atomic force microscopy (AFM) nowadays. Despite of large activities in development of the scanning probe technique, still some challenges remain, namely the chemical analysis on atomic and molecular level.

First, we will present a novel method extending further the chemical analysis [1,2] by means of AFM. Namely we will discuss a new methodology to measure Pauling's electronegativity of individual atoms on surfaces using AFM. Electronegativity has been an important concept in chemistry, originally defined by Pauling as "*the power of an atom in a molecule to attract electrons to itself*". However, its experimental determination on individual surface atoms was not possible so far.

Second, we will discuss the origin of sub molecular AFM/STM resolution acquired with functionalized tips. We will show that the electrostatic force can substantially affect the sub molecular contrast. We will show, that the electrostatic potential on a single molecule can be mapped out with sub molecular resolution.

[1] Y. Sugimoto et al Nature 446, 64 (2007)

[2] M. Setvin et al ACS Nano 6, 6969 (2012)

[3] P. Hapala et al, Phys. Rev. Lett. 113, 226101 (2014)

[4] J. vad der Lit et al, Phys. Rev. Lett. 096102 (2016)

[5] P. Hapala et al. Nature comm. (accepted 2016)

Surface Science
Room 104D - Session SS1+AS+HC+NS-TuM

Surface Dynamics, Non-Adiabaticity, and Theory and Modeling of Surface and Interfacial Phenomena

Moderator: Greg Kimmel, Pacific Northwest National Laboratory

8:00am **SS1+AS+HC+NS-TuM1 Graphene-Semiconductor Catalytic Nanodiodes for Quantitative Detection of Hot Electrons Induced by a Chemical Reaction***, **Hyosun Lee**[*],* KAIST & IBS, Republic of Korea*; I. Nedrygailov,* IBS & KAIST, Republic of Korea*; Y.K. Lee, C. Lee,* KAIST & IBS, Republic of Korea*; H. Choi,* Electronics and Telecommunications Research Institute (ETRI), Republic of Korea*; J.Y. Park,* Institute for Basic Science (IBS) & Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Direct detection of hot electrons produced by exothermic reactions on catalysts is an effective strategy to quantify the non-adiabatic energy transfer during the elementary steps of the surface reactions, which provides an insight of the catalytic activity.[1,2] In particular, hot electron dynamics at the surface of metal nanoparticles (NPs) with precisely controlled shape and size is a challenge as well as a key issue in the real-world catalyst system. Herein, we show a novel scheme of graphene catalytic nanodiode composed of a Pt NPs array on graphene/TiO_2 Schottky nanodiode, which allows detection of hot electron flows induced by hydrogen oxidation on Pt NPs. By analyzing the correlation between the turnover rate (catalytic activity) and hot electron current (chemicurrent) measured on the graphene catalytic nanodiodes, we demonstrate that the catalytic nanodiodes utilizing a single graphene layer for electrical connection of Pt NPs are beneficial for the detection of hot electrons due to not only atomically thin nature of graphene but also reducing the height of the potential barrier existing at the Pt NPs/graphene interface. Thereby, the graphene catalytic nanodiodes offer an effective and easy to use approach to study mechanisms of chemical energy conversion in various heterogeneous system, even including composite catalysts with carbon-based supports.

References

1. H. Lee, I. I. Nedrygailov, Y. K. Lee, C. Lee, H. Choi, J. S. Choi, C. Choi, J. Y. Park, Nano Lett. 16 (2016) 1650-1656.

2. H. Lee, I. I. Nedrygailov, C. Lee, G. A. Somorjai, J. Y. Park, Angew. Chem. Int. Ed. 54 (2015) 2340-2344.

8:20am **SS1+AS+HC+NS-TuM2 Adlayer-Structure Dependent Ultrafast Desorption Dynamics: The Coverage Dependence of Substrate–Adsorbate Energy Transfer in Carbon Monoxide on Pd(111)***, **Sung-Young Hong**,* Brookhaven National Laboratory*; P. Xu,* Stony Brook University*; N.R. Camillone, M.G. White, N. Camillone,* Brookhaven National Laboratory

We have conducted a detailed investigation of the coverage dependence of the ultrafast photoinduced desorption of CO from the (111) surface of palladium. Because the CO binding site depends on coverage, these measurements present an opportunity to examine the dependence of the substrate–adsorbate energy transfer on adsorption site. Specifically, as the CO coverage is increased, the adsorption site population shifts from all three-fold hollow (up to 0.33 ML), to bridge and near bridge (> 0.5–0.6 ML) and finally to mixed three-fold hollow plus top site (0.6 ML to saturation at 0.75 ML). We show that between 0.24 and 0.75 ML this progression of binding site motifs is accompanied by two remarkable features in the ultrafast photoinduced desorption of the adsorbates: (i) a roughly two-orders of magnitude increase in the desorption probability, and (ii) a nonmonotonic variation in the adsorbate–substrate energy transfer rate observed in two-pulse correlation experiments, with a minimum occurring at intermediate coverages. Simulations using a phenomenological model to describe the adsorbate–substrate energy transfer in terms of frictional coupling indicate that these features are consistent with an adsorption-site dependent electron-mediated energy coupling strength, η_{el}, that decreases with binding site in the order: three-fold hollow > bridge and near bridge > top site. The weakening of η_{el} largely counterbalances the decrease in the desorption activation energy that accompanies this progression of adsorption site motifs and moderates what would otherwise be a rise of several orders of magnitude in the desorption probability. Furthermore, we show that within this framework, the observed energy transfer rate enhancement at saturation coverage is due to interadsorbate energy transfer from the copopulation of molecules bound in three-fold hollows to their top-site neighbors. This conclusion is supported by comparison to desorption of CO from mixed CO+O adlayers where the O adsorbs at three-fold hollow sites and further promotes CO desorption from top sites.

8:40am **SS1+AS+HC+NS-TuM3 Evidence for a Spin Accelerated Reaction Mechanism in the Thermal Decomposition of Alkyl Radicals on the Si(100) Surface***, A.J. Pohlman, D.S. Kaliakin, S.A. Varganov,* ***Sean Casey**,* University of Nevada

Density functional theory and complete active space self-consistent field calculations were used to probe the thermal decomposition of alkyl radicals on the Si(100) surface. Single dimer and single row double dimer cluster models were used to mimic the Si(100) surface in the calculations, and results indicate an interdimer β-hydrogen elimination reaction is the kinetically favored thermal decomposition pathway for adsorbed alkyl radicals. This pathway occurs via a spin crossing from the initial singlet energy surface to the triplet surface mediated by spin-orbit coupling. On the triplet surface the barrier to the elimination reaction is predicted to be about 40 kJ/mol lower than on the singlet surface. Experimental thermal desorption studies of alkyl chlorides adsorbed onto the Si(100)-(2x1) surface appear to give desorption energies for alkene products that are consistent with the barriers computed for the interdimer β-hydrogen elimination spin accelerated reaction mechanism. Experimental and computational results for the adsorption/desorption energetics of several different alkyl radicals will be discussed, along with results from partial deuteration studies of adsorption of selected haloalkanes.

9:00am **SS1+AS+HC+NS-TuM4 Hyperthermal Ion Induced Hot Carrier Excitations in a Metal Probed using Schottky Diodes***, **Dhruva Kulkarni**, D.A. Field, D.B. Cutshall, J.E. Harriss, W.R. Harrell, C.E. Sosolik,* Clemson University

We present measurements on hot carrier excitations in a metal irradiated by hyperthermal energy ions.

Specifically, alkali (Na^+/Rb^+) and noble gas(Ar^{q+}) ions were used to irradiate a Schottky diode consisting of

a thin film of Ag (~25nm) grown on an n-type Si (111) wafer. Measurements of the resultant current

through the device were performed as a function of energy, angle of incidence and velocity of the

incident ions. Energy loss of the incident energetic ions inside the metal film leads to the generation of

hot carriers that travel ballistically to the Schottky interface and are detected as a kinetically-induced

---

[*] **National Student Award Finalist**

current or “kinecurrent” within the device. This kinecurrent is analogous to previous measurements of

“chemicurrent” [H. Nienhaus, *Surface Science*, **45**, 1-78 (2002)], which were linked to the energy

delivered to a surface by exothermic reactions that could non-adiabatically couple to the electronic

structure and generate hot carriers.

9:20am **SS1+AS+HC+NS-TuM5 H Atom Scattering, Adsorption, and Absorption in Collisions with Metal Surfaces: the crucial role of electron-hole-pair excitation***, M. Alducin,* Donostia International Physics Center, Spain*; **Daniel Auerbach,*** Max Planck Institute for Biophysical Chemistry, Germany*; M. Blanco-Rey,* Donostia International Physics Center, Spain*; O. Bünermann, Y. Dorenkamp,* Georg-August University of Göttingen*; S.M. Janke,* Max Planck Institute for Biophysical Chemistry, Germany*; H. Jiang,* Georg-August University of Göttingen*; A. Kandratsenka,* Max Planck Institute for Biophysical Chemistry*; G-J. Kroes,* Leiden Institute of Chemistry, The Netherlands*; M. Kammler,* Max Planck Institute for Biophysical Chemistry*; M. Pavenelo,* Leiden Institute of Chemistry **INVITED**

When an H atom collides with a solid surface, it can transfer some of its kinetic energy into elementary excitations of the solid like phonons and electron-hole pairs. If the atom loses enough kinetic energy, it can become bound to the solid, either on the surface or in the bulk. For a metal, the availability of a continuum of low lying electronic excitations can lead to the breakdown of the adiabatic Born Oppenheimer approximation and the facile nonadiabatic excitation of electron-hole pairs (ehp). If the H atom loses sufficient energy, it can enter a bound state with the solid, either on the surface or in the bulk.

We have used a combined theoretical and experimental approach to elucidate the relative roles of adiabatic processes (phonon excitation) and nonadiabatic processes (ehp excitation) in collisions of H atoms with metals, insulators, and graphene. The experiments use photolysis to produce nearly mono-energetic beams of H atoms with energies of 1 - 3.3 eV and high resolution energy loss measurements using Rydberg atom tagging time-of-flight analysis. The theory involves calculations of classical trajectories for H atom collisions with two techniques. In the first, we calculate energies and forces on-the-fly during the course of a trajectory using density functional theory (DFT) and ab initio molecular dynamics (AIMD). In the second, we construct a full dimensional potential energy surface (PES) using a flexible functional form fit to DFT energies and bulk properties of the solid.

The measured mean energy loss for H atoms scattering from metals is large, approximately 30% of the initial energy and there is a tail in the energy loss distribution (ELD) extending to the full energy of incidence. The measured ELD is in reasonable agreement with theory only if nonadiabatic effects are included; adiabatic theory drastically underestimates the energy loss. Scattering from insulators (where ehp excitation can be excluded) shows much smaller energy loss and results consistent with adiabatic theory.

For metals, nonadiabatic effects not only dominate the energy loss process, but also change both the magnitude and mechanism for adsorption on metals. With nonadiabatic effects, the most probable pathway to adsorption is for H atoms to penetrate the surface, lose energy in the subsurface region, and then reemerge to adsorb on the surface.

11:00am **SS1+AS+HC+NS-TuM10 Progress in Characterizing Submonolayer Island Growth: Capture-Zone Distributions, Growth Exponents, and Transient Mobility***, **Theodore L. Einstein,*** University of Maryland, College Park*; A. Pimpinelli,* Rice University*; J.R. Morales-Cifuentes,* Unversity of Maryland, College Park*; D.L. González,* Universidad del Valle, Colombia

Analyzing capture-zone distributions (CZD) using the generalized Wigner distribution (GWD) has proved a powerful way to gain insight into epitaxial growth, in particular to access the critical nucleus size *i*, as reviewed in [1]. The CZ of an island contains all points closer to that island than to any other and is known as a Voronoi tesselation. This approach complements measurements of the growth exponent α from the scaling (with flux *F*) of island density $N \sim F^{\alpha}$ and of the distribution of island sizes. We summarize some extensive Monte Carlo simulations and experiments, especially newer ones, on various systems to which the GWD has been applied. These experiments include atomic or organic adsorbates, sometimes with impurities, and colloidal nano-particles. In some cases, most notably parahexaphenyl (6P) on sputter-modified mica [2], the value *i* extracted from CZD) differs from the [larger] values of *i* deduced from $N \sim F^{\alpha}$. Furthermore, while the scaling was good, the values of α differed considerably at small and large *F*, which was attributed to DLA and ALA dynamics [2]. To reconcile the CZD and scaling measurements, we took into account long-known transient mobility (hot precursors) using a rate-equation approach [3]. We also applied this method to data for pentacene (5A) on the same substrate. In applications of the GWD to social phenomena, notably the areas of secondary administrative units (e.g. counties or French *arrondissements*) [4], lognormal distributions (typically due to multiplicative noise) sometimes arise instead of GWD or gamma distributions; we show this also occurs for some pore-size distributions [5].

*Work at UMD supported by NSF CHE 13-05892

[1] T.L. Einstein, A. Pimpinelli, D.L. González, J. Cryst. Growth **401** (2014) 627; TLE, AP, DLG, J.R. Morales-Cifuentes, J. Physics: Conf. Ser. J. Phys.: Conf. Series **640** (2015) 012024

[2] T. Potocar et al., Phys. Rev. B **83** (2011) 075423 & later work by A. Winkler et al., see [1].

[3] JRM-C, TLE, and AP, Phys. Rev. Lett. **113** (2014) 246101.

[4] R. Sathiyanarayanan, Ph.D. thesis, UMD, 2009; R. Sathiyanarayanan and TLE, preprint.

[5] A.S. DeLoach, B.R. Conrad, TLE, and D.B. Dougherty, submitted.

11:20am **SS1+AS+HC+NS-TuM11 Hindered Translator and Hindered Rotor Models for Calculating the Entropy of Adsorbed Species***, **Lynza H. Sprowl**** [*], Oregon State University*; C.T. Campbell,* University of Washington*; L. Arnadottir,* Oregon State University

Adsorbed species on surfaces are important for a range of applications including heterogeneous catalysis, corrosion processes, and film growth. The need for a fast and accurate way to predict equilibrium constants and rate constants for surface reactions is important for understanding reaction kinetics and for building microkinetic models of catalytic reactions. Here a method to calculate partition functions and entropy of adsorbed species is presented. Instead of using the vibrational frequencies estimated from density functional theory and the harmonic oscillator approximation to calculate the partition function for all modes of motion, we use hindered translator and hindered rotor models for the three modes of motion parallel to the surface, two translations and one rotation. The energy barriers for translation and rotation were determined using density functional theory and the nudged elastic band method for four different adsorbates on a platinum surface: methanol, propane, ethane, and methane. The hindered translator model was used to calculate the entropy contributions from the two translations parallel to the surface and the hindered rotor model was used to calculate the entropy contribution from the rotation about the axis perpendicular to the surface. When combined with the vibrational entropy contributions and the concentration related entropy contributions, this gives the total entropy of the adsorbate on the surface. The total adsorbate entropies were found to agree well with experimental results, with an average absolute value of the error of only 1.1R or 8% for the four adsorbates. This new model should be useful to future researchers in surface chemistry, since it provides more accurate predictions of standard-state entropies and partition functions, and thus more accurate equilibrium constants and rate constants for surface reactions than provided by the standard harmonic oscillator approximation.

11:40am **SS1+AS+HC+NS-TuM12 Stabilization of *X*-Au-*X* Complexes on the Au(111) Surface: A Theoretical Investigation and Comparison of *X*=Sulfur, Chlorine, Methythiolate, and Silylthiolate***, J. Lee, J.S. Boschen, T.L. Windus, P.A. Thiel, J.W. Evans, **Da-Jiang Liu,*** Iowa State University

The involvement of Au atoms in the self-assembled methylthiolate (CH_3S) monolayers on Au(111) has been demonstrated experimentally [1], while for S and Cl, chain-like structures with no direct Au involvement were found [2,3]. We find that for S on various coinage metal surfaces, the linear S-M-S complexes (M=Cu, Ag, Au) are prevalent. A systematical theoretical study of the X-Au-X complexes, with X=S, Cl, CH_3S, and SiH_3S, has been performed using DFT and other quantum chemistry methods. Assuming equilibration of the metal substrate, the chemical potential of X are calculated and used to predict the stability of various Au-X complexes. We find good agreement between DFT and available experimental findings. Furthermore, the van del Waals interaction is shown to play a crucial role in the self-assembly of CH_3S observed in experiments [1].

[1] P. Maksymovych, O. Voznyy, D. B. Dougherty, D. C. Sorescu, J. T. Yates Jr., *Prog. Surf. Sci.***85**, 206 (2010).

---

[*] **Morton S. Traum Award Finalist**

[2] V. V. Zheltov *et al.Phys. Rev. B,* **89**, 195425 (2014).

[3] H. Walen, *J. Chem. Phys.***143**, 014704 (2015).

12:00pm **SS1+AS+HC+NS-TuM13 Contrasting Phonon Confinement and Interface Stability at Fe-Ag and Fe-Cr Multilayers: Insights from *Ab Initio* Calculations***, S. Hong, **Talat Rahman**,* University of Central Florida

We have performed density functional theory based calculations to compare the characteristics of the interface of Fe-Ag and Fe-Cr multilayers. A perfect interface lattice match between the Fe and Ag layers was obtained by rotating fcc Ag(100) layers by 45° on bcc Fe(100). On the other hand, the Fe-Cr interface could be modeled by epitaxial layers of bcc Fe(100) and Cr(100). In Fe-Ag multilayers, we find the signature peak of Fe bulk phonons (35 meV) to be completely diminished, while the low energy peaks are remarkably enhanced, in agreement with experiment [1]. In contrast, the phonon density of state in the Fe-Cr multilayers do not show any salient feature except a slight decrease in the 35 meV peak for the Fe layer at the interface, as compared to that of the middle Fe layer, again in agreement with experiment [2]. The magnetic moment of the interfacial Fe atoms is larger than that of Fe atoms in other layers, as a result of charge transfer from Fe to Ag at the interface. As compared to the middle layers, more spin-up and less spin-down states are occupied at the interface in such a way that Fe donates a large number of spin-down electrons to Ag but receives only a few spin-up electrons from the latter because of the almost fully occupied Ag d-band. This leads to rather unstable Fe-Ag interface. On the contrary, at the Fe-Cr interface, Cr can easily give and take electrons leading to smooth interfacial coupling and stable environment.

[1] B. Roldan Cuenya et al., to be published

[2] Roldan et al, Phys. Rev. B 77, 165410 (2008).

Work supported in part by DOE Grant No. DOE-DE-FG02-07ER46354

Surface Science
Room 104E - Session SS2+AS+HC+NS-TuM
Nanostructures: Growth, Reactivity, and Catalysis

Moderator: Bruce Koel, Princeton University

8:00am **SS2+AS+HC+NS-TuM1 Use of Size Correlations to Probe Reaction Mechanisms on Size-selected Model Catalysts***, **Scott Anderson**,* University of Utah **INVITED**

The ability to prepare model catalysts by deposition of mass-selected metal clusters allows the size and density of catalytic sites to be varied independently and precisely, providing a new tool for mechanistic studies. In addition, preparation of truly monodisperse samples alters the kinetics for Ostwald ripening, thus changing the cluster stability under thermal/reactive conditions. This talk will focus on use of size-dependent correlations between catalytic activity and physical properties such as cluster morphology and electronic properties, to probe the factors that control catalysis and electrocatalysis by supported Pt clusters in the <25 atom size range. The stability of the clusters, and how this varies with size under heating, adsorbate exposure, and potential cycling will also be discussed.

8:40am **SS2+AS+HC+NS-TuM3 Role of the Strong Metal Support Interaction on the Catalytic Activity of Platinum Deposited on TiO_2 Supports***, **R.Paul Hansen**, R.S. Phillips,* University at Albany-SUNY*; E.T. Eisenbraun, C.A. Ventrice, Jr.,* SUNY Polytechnic Institute

Several roadblocks prevent the large-scale commercialization of hydrogen fuel cells, including the stability of catalysts and their substrates and the high cost of the Pt involved in the oxygen reduction reaction (ORR). The former of these problems can be solved by replacing the traditional carbon support with a conductive metal oxide such as reduced TiO_2, which will not easily corrode and should result in longer lasting fuel cells. The Pt is necessary in the cathode of the fuel cell to overcome the slow kinetics of the ORR. In this study, Pt was deposited either by atomic layer deposition (ALD) or physical vapor deposition (PVD). The typical size of the Pt islands that were grown using these deposition techniques was 5-8 nm. One factor that can inhibit the catalytic activity of a metal catalyst on a metal oxide is the strong metal support interaction (SMSI). This is where a metal on a reducible metal oxide can be encapsulated by a layer of the metal oxide support material at elevated temperatures. The processing of materials through atomic layer deposition can exceed this temperature. The TiO_2 substrates used in this study were either grown by ALD, which results in a polycrystalline anatase film, or were single-crystal rutile TiO_2(110) samples prepared in ultra-high vacuum (UHV). The Pt/TiO_2 samples were tested electrochemically using cyclic voltammetry (CV) to determine the level of catalytic activity. To determine the effect of the SMSI interaction on the catalytic activity of the PVD grown samples, CV was performed on samples that were annealed in high vacuum after Pt deposition. Additional characterization was performed with scanning electron microscopy (SEM), Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), and four point probe analysis.

9:00am **SS2+AS+HC+NS-TuM4 Adsorption and Adhesion Energies of Au, Cu, and Ag Nanoparticles on CeO_2(111), MgO(100) and Other Oxide Surfaces***, **Charles T. Campbell**, S.L. Hemmingson, G.M. Feeley,* University of Washington

Heterogeneous catalysts consisting of late transition metal nanoparticles dispersed across oxide supports are ubiquitous in industrial chemistry and energy technology. We have used an ultrahigh vacuum single-crystal adsorption calorimeter to study the adsorption energies of Au, Cu and Ag gas atoms as they adsorb and grow nanoparticles on single-crystal oxide surfaces as models for real catalyst systems. These measurements allow us to determine the chemical potential of metal atoms in supported nanoparticles as a function of particle size and the support upon which they sit. The support effect manifests itself very directly on metal chemical potential via the metal / oxide adhesion energy. Our earlier studies have shown that metal chemical potential can be related to the metal nanoparticle's catalytic activity and deactivation rates through sintering, so there is a great motivation to understand how it varies with particle size and support, and how metal / oxide adhesion energies vary with the nature of the metal and the oxide support material. Through these measurements on a variety of systems, we have discovered systematic trends in these that allow predictions of adhesion energies for system which have not been measured. We have also measured the adsorption energy of isolated Cu atoms on CeO_2(111) terrace sites, which is possible at 100 K. This is the first measurement of the adsorption energy of any late transition metal atom on any oxide surface of the type used as catalyst supports in a situation where the atom sits on the surface as an isolated monomer (as opposed to sitting within a small metal cluster).

9:20am **SS2+AS+HC+NS-TuM5 Effects of Nanoparticles on Surface Resistivity: Ni on Au(111)***, **Joshua Cohen**, R.G. Tobin,* Tufts University

The change in surface resistivity due to the formation of nickel nanoparticles on gold(111) was studied by measuring the resistance of a thin film of Au as a function of Ni coverage, θ. After annealing, Au(111) configures into the herringbone reconstruction and provides a template for the periodic nucleation and growth of Ni nanoparticles. The Ni islands grow radially until θ ~ 0.3 ML, after which, subsequent Ni atoms contribute almost exclusively to a second layer [1].

Surface resistivity arises primarily from the scattering of the substrate's conduction electrons by foreign atoms or defects, and studies of the dependence of surface resistivity on coverage yield insights into growth dynamics, interadsorbate interactions, and interactions between the adsorbed atoms and conduction electrons. For randomly distributed non-interacting scatterers the resistivity change is linear in coverage. Since Ni atoms on Au(111) grow in tight ordered nanoclusters, a nonlinear dependence might be anticipated. Our results, however, show a linear dependence on coverage for Ni atoms in the first layer, as if they were independent point scatterers. At coverages above θ ~ 0.3 ML, there is no further change in resistivity, which we attribute to Ni atoms forming a second layer and making no significant contribution to the surface resistivity.

The samples were 150 nm thick epitaxial Au(111) films on mica prepared by sputtering and annealing in ultrahigh vacuum. The resistance of the film was measured as Ni was thermally evaporated on the surface. Ni coverage was determined using Auger electron spectroscopy (AES), corrected for the inelastic mean free path of the electrons.

The resistance and AES data were analyzed in terms of a growth model that allowed for variation in the coverage at which a second layer begins, the relative probabilities of first- and second-layer growth after that point, and the relative contributions of first- and second-layer Ni atoms to the surface resistivity. The results are consistent with the growth model observed with STM [1], and serve as an indirect probe of the growth kinetics of this interesting system, as well as determining for the first time the contributions of the Ni islands to the surface resistivity of the Au film.

1. Chambliss, D.D., R.J. Wilson, and S. Chiang, *Ordered Nucleation of Ni and Au Islands on Au (111) Studied By Scanning Tunneling Microscopy.* Journal of Vacuum Science & Technology B, 1991. **9**(2): p. 933-937.

9:40am **SS2+AS+HC+NS-TuM6 Three-Dimensional Control of Nanoparticle Layer Deposition by "Click Chemistry"***, **Mackenzie Williams**, A.V. Teplyakov,* University of Delaware

Our previous studies have focused on the formation of highly-controlled nanoparticle mono- and multilayers of silica and magnetic iron oxide nanoparticles through the copper(I) catalyzed azide-alkyne cycloaddition reaction. By using the specific functionalization scheme in that method, we achieved very high surface coverage and the formation of exactly one nanoparticle layer per deposition cycle, as could be observed with scanning electron microscopy (SEM) and atomic force microscopy (AFM). Formation of the triazole ring from the "click" reaction was confirmed by infrared spectroscopy and X-ray photoelectron spectroscopy (XPS), while density functional theory calculations were used to confirm spectroscopic results and investigate the reasons behind the high coverage. In the current work, a higher level of control over the nanoparticle layers is being sought. Conformal filling of the layer over high aspect-ratio features is being studied and would allow this method to be used as a viable alternative to traditional layer-by-layer techniques. Additionally, control of the spatial resolution of the nanoparticle layers upon the substrate via alternative methods of catalysis initiation is currently being investigated.

11:00am **SS2+AS+HC+NS-TuM10 Spherical Metallic Nanostructures Based on Fullerene Scaffolds with Tunable Bandgap, A Scanning Tunneling Microscopy/Spectroscopy (STM/STS) Study***, **Ehsan Monazami**,* University of Virginia*; J.B. McClimon,* University of Pennsylvania*; J.M. Rondinelli,* Northwestern University*; P. Reinke,* University of Virginia

The current literature on annealing of fullerene molecules on tungsten surfaces indicates a complete dissociation of the fullerene cage and the formation of a carbide phase. However, our measurements with high resolution STM and STS illustrate a complex intermediate reaction sequence. Upon annealing of C_{60} adsorbed on a tungsten thin film grown on MgO (001) in UHV, C_{60} does not dissociate and the spherical C_{60} shape is retained up to a temperature of at least 973 K. During the annealing, the band gap of the molecular layer decreases gradually from the wide bandgap of fullerene to a fully metallic electronic state. This transition occurs in a narrow temperature range between 600 K and 700 K. After this transition, the near-spherical particles are termed "nanospheres." This progression was observed with a series of high resolution scanning tunneling spectra and detailed spectral mapping. The bandgap variation presents an approach to achieve the formation of densely packed nanoclusters (nanospheres) with variable bandgap, which are stable at elevated temperatures. Experimental results for sub-ML fullerene coverage on tungsten show that the fullerene molecules are mobile at room temperature, but they become stationary after annealing above 500 K. This immobilization of molecules indicates a strong interaction and likely a covalent bond between the molecule and substrate that is triggered by annealing.

The progression to metallic nanospheres is hypothesized to occur either by gradual substitution of W-atoms or by wetting the molecule with W-atoms and thus formation of W-C bonds in a solid state reaction. These models were tested using density functional theory (DFT) calculations. Two simulation strategies were used. In the first, C_{60} carbon atoms were substituted by W in the molecule and the resulting electronic properties and bandgap were calculated. In the second approach, different adsorption geometries of a C_{60} molecule on the tungsten (110) surface were considered. The variation of the band gap due to different C_{60} orientations relative to the tungsten substrate and various types of hetero-fullerenes will be discussed.

11:20am **SS2+AS+HC+NS-TuM11 Facile Synthesis of Gold Nanoworms and their Excellent Surface Enhanced Raman Scattering (SERS) and Catalytic Properties***, **Waqqar Ahmed**,* COMSATS Institute of Information Technology, Pakistan*; J.M. van Ruitenbeek,* Leiden University, Netherlands

Gold nanoparticles exhibit interesting optical properties because of the surface plasmon resonance. The shape and size of gold nanoparticles can markedly influence their optical properties. A spherical nanoparticle has a single palsmon peak, while rod-shaped nanoparticles have two plasmon peaks because of their shape anisotropy. Furthermore, slight deviations from the rod morphology can markedly influence the optical properties. For example, worm-shaped gold nanoparticles can have more than two plasmon peaks. Moreover, nanoworms can display very high local field enhancements upon plasmon excitation owing to their special shape and surface roughness.

We have devised a simple, seedless, high-yield protocol for the synthesis of gold nanoworms [1]. Nanoworms were grown simply by reducing $HAuCl_4$ with ascorbic acid in a high pH reaction medium in the presence of growth directional agents. In contrast to the seed-mediated growth of gold nanorods where a seed particle grows into a nanorod, nanoworms grew by oriental attachment of nanoparticles. By varying different reaction parameters we were able to control the length of NWs from a few nanometers to micrometers. Furthermore, the aspect ratio can also be tuned over a wide range.

Owing to their special morphology, gold nanoworms are much superior than the conventional nanorods for numerous applications. For instance, we have seen that they show markedly superior SERS and catalytic properties compared to their nanorod counterparts. This is due to their high-energy rough surface and twisted shape, which not only provides an ideal platform for catalytic activities but also generates local hot-spots upon plasmon excitation. Our study shows that both catalytic and SERS properties of gold nanoworms are strongly dependent on their length.

[1] W. Ahmed, C. Glass, and J.M. van Ruitenbeek, *Nanoscale*, 6, 13222, (2014)

11:40am **SS2+AS+HC+NS-TuM12 Surface Hydrogen Enables Sub-Eutectic Vapor-Liquid-Solid Semiconductor Nanowire Growth***, S.V. Sivaram, H. Hui,* Georgia Institute of Technology*; M. de la Mata, J. Arbiol,* Catalan Institute of Nanoscience and Nanotechnology, Spain*; **Michael Filler**,* Georgia Institute of Technology

Semiconductor nanowires are emerging as indispensable nanoscale building blocks for next generation energy conversion, electronic, and photonic devices. The bottom-up vapor-liquid-solid (VLS) mechanism – whereby a liquid eutectic "catalyst" droplet collects precursor molecules (or atoms) from the vapor and directs crystallization of the solid nanowire – is a nearly ubiquitous method for nanowire synthesis. While VLS growth below the bulk metal-semiconductor eutectic temperature has long been known, the fundamental processes that govern this behavior are poorly understood. Here, we show that hydrogen atoms adsorbed on the Ge nanowire sidewall enable AuGe catalyst supercooling and control Au transport. Our experimental approach combines in situ infrared spectroscopy to directly and quantitatively determine hydrogen atom coverage with a "regrowth" step that allows catalyst phase to be determined with ex situ electron microscopy. Maintenance of a supercooled catalyst with only hydrogen radical delivery confirms the centrality of sidewall chemistry. This work underscores the importance of the nanowire sidewall and its chemistry on catalyst state, identifies new methods to regulate catalyst composition, and provides synthetic strategies for sub-eutectic growth in other nanowire systems. We leverage this newfound understanding of nanowire growth chemistry to fabricate large-area arrays of high quality axial Si/Ge heterostructures for the first time.

12:00pm **SS2+AS+HC+NS-TuM13 Ultrafine Sodium Titanate Nanowires with Extraordinary Strontium Ion-Exchange Property***, **Koji Nakayama**,* Tohoku University, Japan

The removal of radioactive substances released to the environment by a nuclear accident is an emergent issue. The water treatment based on the ion exchange process is the most effective decontamination technology, and inorganic ion exchangers, titanates, have been used for the capture of Sr ions owing to their high radiation stability and extreme ion selectivity. However, the reported adsorption capacity and ion exchange efficiency are not satisfied. We show the formation of sodium titanate nanowires with a few nanometers in diameter, having a mogul-shaped surface, forming hierarchically a three-dimensional network skeletal structure, and exhibiting remarkable Sr ion exchange properties [1]. They are produced by unique and simple non-thermal processes through the simultaneous selective leaching of Al and oxidation of Ti in a rapidly solidified Ti-Al alloy ribbon in NaOH solution. The experimental saturated adsorption capacity is tripledand the uptake rate is at least three hundredtimes faster than these of the previous reports. The results demonstrate that the newly created nanowires exhibit a potential application in the decontamination and disposal of nuclear waste.

[1] Y. Ishikawa, S. Tsukimoto, K. S. Nakayama, and N. Asao, Nano Lett. **15**, 2980-2984 (2015).

Applied Surface Science
Room 101B - Session AS+SS-TuA

Data Analytics in Surface Science and Nanoscience

Moderators: Anders Mikkelsen, Lund University, Sweden, Petra Reinke, University of Virginia

2:20pm **AS+SS-TuA1 Fast Strain Mapping of Nanowire Light-Emitting Diodes Using Nanofocused X-ray Beams***, T. Stankevic,* Copenhagen University, Denmark*; U. Johansson, L. Samuelson,* Lund University, Sweden*; G. Falkenberg,* DESY, Hamburg, Germany*; R. Feidenhans'l,* Copenhagen University, Denmark*; **Anders Mikkelsen,*** Lund University, Sweden

Nanofocused X-ray beams are nondestructive probes that uniquely allow direct measurements of the nanoscale strain distribution and composition found at the interfaces and surfaces inside the micrometer thick layered structures ofmany electronic device architectures [1]. While the method has generally been considered time consuming, we demonstrate that by special design of X-ray nanobeam diffraction experiment we can (in a single 2D scan with no sample rotation) measure the individual strain and composition profiles of many structures in an array of upright standing nanowires[2]. We make use of the observation that in the generic nanowire device configuration, which is found in high-speed transistors, solar cells, and light-emitting diodes, each wire exhibits very small degrees of random tilts and twists toward the substrate. Although the tilt and twist are very small, they give a new contrast mechanism between different wires. In the present case, we image complex nanowires for nanoLED fabrication and compare to theoretical simulations, demonstrating that this fast method is suitable for real nanostructured devices.

We then go on to discuss the complications of data analysis as the amount of data available is dramatically increased with the advent of new highly coherent synchrotrons such as MAX IV in Lund Sweden [3] and improved experimental setups[2,4,5]. Using several detectors that give both real space fluorescence and 2D diffraction information combined with scanning both translational, rotational and time coordinates for in operando and in-situ studies in 3D - an enormous multidimensional dataset can be created in a few days. To fully retrieve all the information inside such dataset and pushing resolution and sensitivity limits new computational methods are needed in combination with advanced modelling.

[1] E. Lind et al., IEEE J. El. Dev. Soc. 3, 96 (2015); J. Wallentin et al., Science 339, 1057 (2013).

[2] T. Stankevic et al, ACS Nano 9 (2015) 6978

[3] " Ultimate upgrade for US synchrotron", Nature 501 (2013) 148

[4] U. Johansson, U. Vogt, A. Mikkelsen, Proc. SPIE 8851, X-Ray Nanoimaging: Instruments and Methods, 88510L (September 26, 2013); doi:10.1117/12.2026609

[5] T. Stankevic et al. Appl. Phys. Lett. 107 (2015) 103101

2:40pm **AS+SS-TuA2 Bellerophon Environment for Analysis of Materials (BEAM), A High Performance Computing Workflow Platform for Materials Research***, E.J. Lingerfelt, A. Belianinov, E. Endeve,* Oak Ridge National Laboratory*; O.S. Ovchinnikov,* Vanderbilt University*; S. Somnath, R.K. Archiblad, S.V. Kalinin, **Stephen Jesse,*** Oak Ridge National Laboratory

Improvements in scientific instrumentation allow imaging at mesoscopic to atomic length scales, many spectroscopic modes, and now—with the rise of multimodal acquisition systems and the associated processing capability—the era of multidimensional, informationally dense data sets has arrived. Technical issues in these combinatorial scientific fields are exacerbated by computational challenges best summarized as a necessity for drastic improvement in the capability to transfer, store, and analyze large volumes of data. The Bellerophon Environment for Analysis of Materials (BEAM) platform provides material scientists the capability to directly leverage the integrated computational and analytical power of High Performance Computing (HPC) to perform scalable data analysis and simulation via an intuitive, cross-platform client user interface. This framework delivers authenticated, "push-button" execution of complex user workflows that deploy data analysis algorithms and computational simulations in HPC environments like Titan at the Oak Ridge Leadership Computing Facility (OLCF).

Here, we address the underlying HPC needs for characterization in the material science community, elaborate how BEAM's design and infrastructure tackle those needs, and present a small sub-set of user cases where scientists utilized BEAM across a broad range of analytical techniques and analysis modes. BEAM system will be demonstrated for 4D Ronchigram analysis and property extraction of atomically resolved STEM (Scanning Transmission Electron Microscopy) data, parallel spectroscopic curve fitting in SPM (Scanning Probe Microscopy) data, and image segmentation.

Acknowledgements

This work is partially supported by the Laboratory Directed Research and Development (LDRD) program at ORNL, which is managed by UT-Battelle, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC05-00OR22725 (E.J.L., A.B., E.E., O.O., S.S., C.T.S., S.V.K., M.S., and S.J.). This research was conducted at the Center for Nanophase Materials Sciences and the Spallation Neutron Source, which are DOE Office of Science User Facilities. Research by J.M.B. is supported by the Center for Accelerating Materials Modeling (CAMM), which is funded by DOE Basic Energy Sciences under FWP-3ERKCSNL. This research used resources of ORNL's Compute and Data Environment for Science (CADES) and the Oak Ridge Leadership Computing Facility (OLCF), which are supported by the Office of Science of the U.S. Department of Energy under Contract No. DEAC05-00OR22725. The mathematical aspects were sponsored by the applied mathematics program at the DOE by the ACUMEN project.

3:00pm **AS+SS-TuA3 The Center for Advanced Methods for Energy Research Applications (CAMERA):Mathematical Methods for Data Science from Experimental Facilities***, **James Sethian,*** University of California at Berkeley **INVITED**

The Center for Advanced Methods for Energy Research Applications (CAMERA), jointly funded by the U.S. Department of Energy Offices of Advanced Scientific Research (ASCR) and Basic Energy Sciences (BES), focuses on mathematical models, algorithms, and codes thatanalyze, interpret, and understand the information contained within experimental data, particularly arising from light sources and nanoscale facilities. Initial focus areas include ptychography, tomography, grazing incidence small-angle scattering, image analysis and reconstruction methods, fluctuation scattering, single particle imaging, fast electronic structure methods, and automatic materials characterization and design. In this talk, we will describe the structure of CAMERA, and summarize some of the major projects. In particular, we will discuss work on: (1) Algorithms for real-time streaming ptychography. Ptychographical phase retrieval is a non-linear optimization problem, made tractable through exploiting redundancy inherent in obtaining diffraction patterns from overlapping regions of the sample. Here, we describe SHARP: our "Scalable Hetereogeneous Adaptive Real-time Ptychography" framework that enables high-throughput streaming analysis. (2) New algorithms for fluctuation scattering and single particle imaging: In single particle diffraction (SPD) imaging, a large number of X-ray diffraction images are collected from individual particles, which are delivered to an ultrabright X-ray beam at random and unknown orientations through either a liquid droplet or aerosol delivery system. Recently, a new mathematical and algorithmic procedure has been introduced, known as "Multi-tiered Iterative Phasing" (MTIP), which simultaneously determines the orientations, 3D intensity function, complex phases, and the underlying molecular structure together in a single iterative process. (3) Machine learning methods for classification and characterization of scattering patterns. Grazing Incidence Small Angle X-ray Scattering (GISAXS) is an important reciprocal-space imaging modality which provides statistical information about a sample in 3-D. GISAXS is widely used for studying thin films that play a vital role as building blocks for the next generation of renewable energy technology. One challenge in GISAXS imaging is to be able to accurately infer properties of the material such as the crystal lattice corresponding to the sample from a single 2-D diffraction/scatter patterns. We will discuss our work using machine learning algorithms and convolution neural net classifiers to automatically provide structural details about the sample by analyzing the measured GISAXS diffraction patterns.

4:20pm **AS+SS-TuA7 New Data Analysis Tools for X-ray Photoelectron Spectroscopy (XPS) and Spectroscopic Ellipsometry (SE)***, **Matthew Linford**, B. Singh, J. Bagley,* Brigham Young University*; J. Terry,* Illinois Institute of Technology*; A. Herrera-Gomez,* CINVESTAV-Unidad, Mexico

Here we discuss a series of new data analysis tools for X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry (SE). For XPS, these include uniqueness plots, and the equivalent and autocorrelation widths. For SE, they include distance, principal component, and cluster analyses. Uniqueness plots are widely used in the SE community for identifying correlation between fit parameters. They are easily interpreted. However, they appear not to have been employed for XPS data analysis. And certainly better tools are needed to identify inappropriate peak fits to XPS narrow scans because (i) XPS is now receiving in excess of 10,000 mentions in the literature each year, and (ii) with the proliferation of the technique, the number of untrained users that are collecting and fitting data has significantly increased. In a number of reported peak fits, too many fit parameters have been introduced into the data modeling, which has reduced or eliminated the statistical meaning of these parameters. Uniqueness plots show the error of a fit as a function of one of the variables in that fit, where the values of a specified variable are systematically fixed to quantities about its optimal value. If the same, low error can be obtained for all the values of the variable in question, a horizontal line is obtained, which signals fit parameter correlation. Here, the same error is obtained because other variables in the fit can compensate for the systematic change to the variable in question. In contrast, if the error in the fit rises as the variable in question is systematically changed about its optimal value, the fit has uniqueness. Uniqueness plots that indicate the absence of fit parameter correlation are often parabolic in shape. We have applied uniqueness plots to the peak fitting of XPS C 1s narrow scans of ozone-treated carbon nanotube (CNT) forests that were obtained as part of a study on CNT-templated thin layer chromatography plates, and Si 2p narrow scans of oxidized silicon. In both cases, uniqueness plots showed that unconstrained fits had poor uniqueness, while more reasonably constrained fits had better uniqueness. These results indicate that uniqueness plots may be a valuable tool for identifying inappropriate peak fits in XPS. In this presentation, I will also briefly mention the use of the equivalent and autocorrelation widths in analyzing XPS narrow scans, and then focus on distance, principal component, and cluster analyses in SE data analysis. Our recent (2016) paper on this topic appears to be only the second example of the application of chemometrics to SE data analysis in the literature.

4:40pm **AS+SS-TuA8 A Surface Investigation of Parchments using ToF-SIMS and Principle Component Analysis***, **Marie-Laure Abel**, J.F. Watts, V. Vilde,* University of Surrey, UK

Parchments are an historical writing support mostly used during the Middle Ages. Their popularity dates from the second century before Christ (BC) in Pergame, Turkey, from which the name originates. Unlike paper, parchment is made of animal skin with a process similar to that used to produce leather. The products used in the fabrication vary and any animal species can be used, although most historical parchments are made from sheep, goat and calf. Information of species recognition on parchments is currently provided either using proteomics or DNA analysis. However each technique presents difficulties and sometimes it is not possible to obtain an unambiguous result. Many valuables manuscripts are written on parchment such as the Magna Carta or the Codex Sinaiticus, which justifies the effort put towards the study of this material in order to improve the conservation process and to learn more about its history.

In this work, a new technique was used in order to assess if any information may be gleaned and help in the process of recognition or even providing any further information to conservators to be used for preservation of historical parchment. Time of flight secondary ion mass spectrometry (ToF-SIMS) has been applied to the analysis of parchment specimens. Indeed while ToF-SIMS has been previously applied to a variety of samples of some significance in the cultural heritage field such as paintings or mummies, it has not been applied to parchments. To facilitate the data treatment process, this has been coupled with data analysis using chemometrics, namely principle component analysis (PCA).

A series of specimens of various ages and species were analysed on both sides, "skin" and "flesh". These samples included sheep, goat and calf. In addition, an unknown sample was also introduced to ascertain if its characteristics could be shown to be close to any species. Results indicate that it is fairly straightforward to distinguish between goat and sheep while calf is more difficult to separate from other species which is unexpected as biologically goat and sheep are considered the closest species within the selection. Furthermore the unknown specimen exhibits data which would classify it as a goat specimen. Considering the sides examined separations are seen within one particular species but the direction of the variation is not the same from one species to another. More work is needed to ascertain which side is being analysed for any unknown materials as the behaviour varies amongst the species examined in this work.

5:00pm **AS+SS-TuA9 Multivariate Analysis of Very Large Hyperspectral SIMS Datasets: What Can We Do, and What Would We Like to Do?***, **Henrik Arlinghaus**,* ION-TOF GmbH, Germany **INVITED**

Advances in instrumentation capabilities, as well as increases in the complexity of modern materials have resulted in a corresponding increase in the size and complexity of data acquired during sample analysis. The increase in the spatial and spectral resolution of the instrumentation is nominally a boon to the analyst, as the measured data more accurately depicts the sample. However, the resulting hyperspectral images routinely consist of upwards of ten thousand pixel spectra for 2D analyses (e.g. a 128x128 pixel image), or millions of voxel spectra for 3D analyses, each of which may consist of hundreds or thousands of ion peaks. Because of the sheer amount of information contained within such an image, it is often no longer feasible to conduct a full manual analysis of the data. An additional factor exacerbating this issue is the fact that many studies necessitate the analysis of a series of spatially resolved replicate measurements of a single sample, or of multiple similar samples. In these studies the aim is not only to characterize the contents of each individual measurement, but also to determine the similarities and differences between the measurements, while ignoring subtle differences caused by changes in analysis conditions between the individual measurements.

A solution to the problem of information overload is the use of multivariate analysis techniques to help guide the analyst, in order to reduce the time needed for determining the chemical make-up of the analyzed samples. These techniques use different approaches in order to reduce the dimensionality of the measured data, resulting in a small set of factors which recreate a simplified model of the data.

The use of MVA approaches, such as Principal Component Analysis (PCA) and Maximum Autocorrelation Factors (MAF), has become an established method of simplifying the analysis of SIMS data arising from a single measurement. We will discuss alternatives to these commonly used methods, including new variations of Multivariate Curve Resolution (MCR) which use additional optimization criteria, as well as MVA approaches not commonly used in SIMS data analysis. Additionally, we will discuss the unique challenges which may arise when applying MVA techniques to the full hyperspectral data contents of a series of measurements.

5:40pm **AS+SS-TuA11 High mass-resolution 3D ToF-SIMS: PCA and visualization in seconds using Graphical Processor Units (GPUs)***, **Peter Cumpson**, I.W. Fletcher, N. Sano, A.J. Barlow,* Newcastle University, UK

Multivariate analysis offers the exciting prospect of unlocking the information content of 3D SIMS of complex organic and biological samples with sub-micron resolution. However applying principal component analysis (PCA) to large images or 3D imaging depth-profiles has been difficult until now because of the Gb to Tb size of the matrices of data involved. The result has always been an "out of memory" error.

Recently[1] we applied two algorithms, RV1 and RV2, originally developed by Halko *et al*[2] that improve the speed of PCA and allow datasets of unlimited size respectively, even on ordinary personal computers. In this presentation we show results of applying these algorithms to perform PCA on full 3D ToF-SIMS data of several examples of plant and small animal tissue. The datasets we process in this way are typically 128x128 or 256x256 pixel depth-profiles of around 100 layers, each voxel having a 70,000 value mass spectrum associated with it, giving datasets of at least 1Tb in size when uncompressed. These data were acquired using our Ionoptika J105 and Iontof IV instruments, with Helium Ion Microscope images of particular key features.

Even for such large datasets a rapid PCA calculation is often needed during analysis sessions to inform decisions on the next analytical step. We have therefore implemented the RV1 algorithm on a PC having a Graphical Processor Unit (GPU) card containing 2,880 individual processor cores[3]. This increases the speed of calculation by a factor of around 4 compared to what is possible using the fastest commercially-available desktop PCs, and full PCA is now performed in less than 7 seconds.

We then use the GPU to allow real-time interactive visualization of the principal components in 3D. This leads to some spectacular and information-rich tomographic images that can be an excellent basis for discussion between analysts and the biologists and medics who understand the morphology and anatomy of their tissue samples.

[1] P J Cumpson *et al*, *Surf. and Interface Anal*. **47** (2015) 986-993.

[2] N P Halko et al, *SIAM Review,Survey Rev. Sec.* 53 (2011) 217–288.

[3] P J Cumpson et al, *Surf. and Interface Anal*., onlinelibrary.wiley.com/doi/10.1002/sia.6042/full

6:00pm **AS+SS-TuA12 Mass Spectrometry Image Fusion*, Bonnie June Tyler,*** Universität Münster, Germany*; H.F. Arlinghaus,* University of Muenster, Germany

As mass spectrometry imaging (MSI) has moved from the technique development stage into real world biological studies, the need to combine mass spectrometry images with other biologically relevant imaging techniques has become important. Techniques as diverse as electron microscopy, scanning probe microscopy, XPS imaging, H&E staining, and fluorescent labeling can provide important information that is complementary to the mass spectral images. Combining the information from these complementary measurements is often necessary for accurate understanding of biological samples. Within the field of mass spectrometry imaging alone, combining different imaging modes, such as MALDI/ToF-SIMS, or GCIB ToF-SIMS/LMIG ToF-SIMS, can enhance understanding of the specimens being studied.

In theory, more data should enable more confident conclusions. In practice, however, the challenges of handling and reducing very large imaging data sets, that have disparities in spatial resolution and contrast mechanisms, can result in biased or misleading conclusions. In order to facilitate more consistent, accurate and useful descriptions of real world samples, advanced data exploration tools are needed. Image fusion is an approach to combining data from different sources that is receiving increasing attention within the field of mass spectrometry imaging.

Although many algorithms for image fusion have been developed for applications in remote sensing, medical imaging and photography, the distinctive features of mass spectrometry make many of these techniques inappropriate for use in this field. We have tested algorithms from two major classes of image fusion, those that operate in the spatial domain and those that operate in the frequency domain. Common artefacts caused by the different algorithms have been identified. Two modified algorithms have been developed which can be used to produce satisfactory fused images using mass spectrometry data. The first approach combines multivariate analysis (MVA) and discreet cosine transform (DCT) and is useful for combining MSI images with monochromatic images. The second algorithm, which uses a combination of multivariate methods, is useful for fusing MSI data with a second spectral image. Both of these new image fusion approaches have been tested on simulations, model systems and real tissue samples. We have shown that MVA image fusion can be a valuable technique for reducing noise, improving image contrast and enhancing the sharpness of mass spectrometry images. With appropriate attention to the distinctive features of each imaging method, image fusion can be done without significant artefacts or distortion of the spectral detail.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-TuA

Probing Spin-Dependent Phenomena

Moderators: Phillip First, Georgia Institute of Technology, Shivani Rajput, Oak Ridge National Laboratory

2:20pm **SP+AS+MI+NS+SS-TuA1 Spin Sensing and Magnetic Design at the Single Atom Level*, Alexander Khajetoorians,*** Radboud University, The Netherlands **INVITED**

Unraveling many of the current dilemmas in nanoscience hinges on the advancement of techniques which can probe the spin degrees of freedom with high spatial, energy, and ultimately high temporal resolution. With the development of sub-Kelvin high-magnetic field STM, two complementary methods, namely spin-polarized scanning tunneling spectroscopy (SP-STS) [1] and inelastic STS (ISTS) [2-3], can address single spins at the atomic scale with unprecedented precession. While SP-STS reads out the projection of the impurity magnetization, ISTS detects the excitations of this magnetization as a function of an external magnetic field. They are thus the analogs of magnetometry and spin resonance measurements pushed to the single atom limit. We have recently demonstrated that it is possible to reliably combine single atom magnetometry with an atom-by-atom bottom-up fabrication to realize complex atomic-scale magnets with tailored properties [4-6] on metallic surfaces [1,7]. I will discuss the current state of the art of this growing field as it pertains to single spin information storage, and how the functionality of coupled magnetic adatoms can be tailored on surfaces by substrate mediated interactions. I will discuss our recent efforts toward realizing tailored chiral magnets [8] and present an outlook on future perspectives toward probing quantum matter at ultra-low temperatures.

[1] A.A.K., et al., PRL, 106, 037205 (2011); [2] A. J. Heinrich, et al., Science, 306, 466 (2004); [3] A.A.K, et al., Nature, 467, 1084 (2010); [4] A.A.K., et al., Nature Physics, 8, 497 (2012) [5] A.A.K., et al., Science, 332, 1062 (2011), [6] A.A.K., et al., Science, 339, 55 (2013), [7] A.A.K., et al., PRL, 111, 126804 (2013). [8] A.A.K., et al. Nature Comm, 7, 10620 (2016).

3:00pm **SP+AS+MI+NS+SS-TuA3 Electron Spin Resonance of Single Atom and Engineered Spin Structures*, Taeyoung Choi,*** *W. Paul, C.P. Lutz, A.J. Heinrich,* IBM Almaden Research Center **INVITED**

The scanning tunneling microscope (STM) has been one of the most versatile tools for atomic-scale imaging, manipulation, and tunneling spectroscopy. Inelastic spin excitation and spin-polarized tunneling have been employed to study spin physics of individual atoms and engineered structures, demonstrating nanoscale memory bits [1] and logic gates [2]. However, the energy resolution of the STM is mainly limited by a temperature of a system surrounding the atomic spins (>100 µeV).

Here, we successfully combine electron spin resonance (ESR) and STM, coherently driving spin resonance of individual iron (Fe) atoms on surfaces (MgO/Ag(100)) [3]. A radio-frequency electric field (~20 GHz), applied at the tunneling junction, modulates the spin state of the Fe atoms. The spin resonance signal is detected by a spin-polarized tunneling current. The ESR signals from individual Fe atoms differ by a few GHz (~10µeV) while the ESR linewidth is in the range of only a few MHz (~10neV). Such a high energy resolution enables us to distinguish spin distributions down to single-atom level and to investigate weak magnetic interactions.

When we placed two Fe atoms close together with controlled atom manipulation, we found that the ESR signal from each Fe atom splits into doublet, of which separation depends on the distance between two atoms. Our measurements show $r^{-3.024\pm0.026}$ distance-dependent splitting, in excellent agreement of magnetic dipole-dipole interaction. We utilized this precisely measured dipolar interaction to determine the location and magnetic moment of unknown spin centers with sub-angstrom and one hundredth of Bohr magneton precision [4].

Coherent quantum control of individual atoms on surfaces combined with atom manipulation may promise the STM as a new and unique platform for a quantum sensor, investigating spin-labeled molecular structures and a quantum information processor, modeling quantum magnetism.

We gratefully acknowledge financial support from the IBM and Office of Naval Research.

[1] S. Loth, S. Baumann, C.P. Lutz, D.M. Eigler, A.J. Heinrich, Science **335**, 196 (2012).

[2] A.A. Khajetoorians, J. Wiebe, B. Chilian, and R. Wiesendanger, Science **332**, 1062 (2011).

[3] S. Baumann*, W. Paul*, T. Choi, C.P. Lutz, A. Ardavan, A.J. Heinrich, Science **350**, 417 (2015).

[4] T. Choi et al., *manuscript in preparation.*

4:40pm **SP+AS+MI+NS+SS-TuA8 Controlling Kondo Effect of Magnetic Molecules on Au(111) by Small Molecule Binding*, MinHui Chang,*** *S.J. Kahng,* Korea University, Republic of Korea*; Y.H. Chang,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea*; H.W. Kim, S.H. Lee,* Korea University, Republic of Korea*; Y.-H. Kim,* KAIST, Republic of Korea

Controlling and sensing spin states of magnetic molecules at the single molecule level is essential for spintronic molecular device applications. Here, we demonstrate that spin interactions of Co-porphyrin on Au(111) can be controlled by adsorption and desorption of small molecules, and be sensed using scanning tunneling microscopy and spectroscopy (STM and STS). Bare Co-porphyrin showed a clear zero-bias peak, a signature of Kondo effect in STS, whereas Co-porphyrin adsorbed small molecules showed modified zero-bias peaks, with reduced full width half maximum or Kondo temperature. Our density functional theory calculation results explain it with spatial redistribution of unpaired spins in d_z2 Orbitals. Our study opens up ways to tune molecular spin interactions by means of chemical binding.

5:00pm **SP+AS+MI+NS+SS-TuA9 Spin-polarized Scanning Tunneling Microscopy on Surfaces Prepared by Molecular Beam Epitaxy*, Arthur Smith,*** Ohio University Nanoscale and Quantum Phenomena Institute **INVITED**

Spin-polarized scanning tunneling microscopy (SP-STM) has proven to be a powerful *in-situ* technique for obtaining detailed information about spin structures at surfaces down to atomic scale.[1] It has been applied extensively to investigate pristine ferromagnetic and antiferromagnetic (aFM) transition metal surfaces, with many great results in the case of model systems such as nano-sized magnetic islands and single magnetic monolayers.[2] This has led to fascinating discoveries of nanoscale magnetic domains, domain walls, spin spirals, spin skyrmions, and much more.[3,4] Although not simple in practice, SP-STM can in principle also yield unprecedented spin characterization on a broad spectrum of material surfaces, including practical, real world systems. For example, it could be applied to investigate surfaces of intermetallic compounds, superconductors, complex magnetic oxides, and magnetic semiconductors.

We are applying SP-STM to study various magnetic systems grown *in-situ* by molecular beam epitaxy, including transition metal nitrides,[5] magnetic-doped nitride semiconductors, and several bi-metallic magnetic systems. I will present our recent work using STM and SP-STM, beginning with a discussion of manganese nitrides, including our work on aFM θ-phase MnN and ferrimagnetic ε-phase Mn_4N. The θ-phase films are very complex due to the expectation of canted spins within each atomic layer with four unique canting angles, while the ε-phase films contain two types of spins (Mn^I and Mn^{II}) with equally complex spin arrangements.

A second material we are working on is the chromium nitride system in which we investigate its electronic and spin properties in a low-temperature SP-STM system. Spectroscopy results to date suggest a *d*-wave resonance on the surface and a Kondo signature for nanoscale iron islands grown on atomically-smooth CrN surfaces.

I will also present results for Mn δ-doped semiconducting gallium nitride surfaces in which we find atomic layer ferromagnetism within a unique and stable √3 x √3 - R30° MnGaN surface reconstruction. Spectroscopy clearly reveals spin-polarized and spin-split Mn states, as predicted by first principles theory calculations. SP-STM measurements map out ferromagnetic domains at *room temperature*, and the additional presence of magnetic rim states seen at the edges of ferromagnetic islands, as well as magnetic hysteresis, give further interest to this intriguing system.

[1] R. Wiesendanger, Rev. Mod. Phys. **81**, 1495 (2009).

[2] M. Bode et al., Phys. Rev. Lett. **92**, 67201 (2004).

[3] P. Ferriani et al., Phys. Rev. Lett. **101**, 027201 (2008).

[4] S. Loth et al. Science **335**, 196 (2012).

[5] K.K. Wang and A.R. Smith, Nano Lett. **12**, 5443 (2012).

5:40pm **SP+AS+MI+NS+SS-TuA11 The Use of Scanning Probe Techniques to Study the Behaviour of Second Phase Particles in Beryllium and Their Role in Localised Corrosion***, **Christopher Mallinson**, J.F. Watts,* University of Surrey, UK

Scanning Kelvin probe force microscopy (SKPFM) has been employed to examine the galvanic activity of a wide range of second phase particles in S-65 beryllium that are believed to have a role in the localised corrosion of the metal. SKPFM and AFM analysis has been combined with additional surface and bulk analysis techniques of scanning electron microscopy, energy dispersive x-ray spectroscopy and Auger electron spectroscopy to provide a detailed overview of the link between the bulk and surface composition of particles and their Volta potential or surface contact potential.

Initial results appear to show that all second phase particles are more noble than the beryllium matrix with the greatest potential difference observed for $AlFeBe_4$ and alumina or carbide like particles. The more negative Volta potential indicates that the particles should act as local cathodes when the metal is exposed to an aqueous environment.

The initial investigation, which is being performed in-air, will be expanded to determine the effect of increasingly higher humidity environments on the behaviour of the particles. It is hoped that this will provide a greater understanding about the onset of pitting corrosion in beryllium.

6:00pm **SP+AS+MI+NS+SS-TuA12 Many-body Interaction induced Spin-split States of Single Vacancy in Graphite***, **Wonhee Ko**,* Samsung Advanced Institute of Technology, Republic of Korea*; H.W. Kim, Y. Cho,* Samsung Advanced Institute of Technology*; Y. Kuk,* Seoul National University, Korea, Republic of Korea*; S.W. Hwang,* Samsung Advanced Institute of Technology

Although carbon atoms have no magnetic states, it has been known that defects in graphene or graphite can have magnetic states induced by many-body interaction. By utilizing ultra-low-temperature scanning tunneling microscopy, we observed the spin-split states of single vacancy in graphite, which is a hallmark of magnetic states. Evolution of the spin splitting in the magnetic field did not follow the Zeeman effect of single electron states, and can be explained only when we consider electron-electron interaction. Quantitative analysis showed that the strength of the electron-electron interaction is in the range of 1~3 meV. Our observation implies that the simplest defect in graphite like single vacancy can behave as magnetic, which would be an important ingredient for development of carbon-based spintronic devices.

Surface Science
Room 104E - Session SS+AS-TuA

Structure and Characterization of Oxides

Moderator: Robert Bartynski, Rutgers, the State University of New Jersey

2:20pm **SS+AS-TuA1 Phase Formation and Stability of Reactive Sputtered Zirconium Dioxide Thin Films***, **Mohsin Raza**, D. Cornil, J. Cornil,* University of Mons, Belgium*; S. Lucas,* University of Namur, Belgium*; A.L. Thomann, A. Caillard, M. El Mokh,* GREMI CNRS/Université d'Orléans, France*; J.F. Pierson, P. Boulet,* Université de Lorraine, France*; R. Snyders, S. Konstantinidis,* University of Mons, Belgium

As materials properties are greatly influenced by their phase constitution, therefore it's of high importance to understand and address the mechanisms driving their phase formation and stability. In this respect, zirconium oxide (ZrO_2) has been the focus of a special attention for the last couple of decades regarding the stabilization of its cubic (c) phase at room temperature.

In the present study, the role of the film chemistry i.e. of oxygen vacancies and of energy deposited during the film growth is investigated. To this purpose, 100 nm thick films of zirconium oxide are grown in the poisoned mode as well as in the transition zone with the help of voltage feedback control unit (Speedflo mini from Gencoa UK). During the film growth, to have a fast response from the feedback unit and thus a tight control over the film chemistry (i.e. O/Zr ratio), oxygen is injected just at the target surface. By systematically varying the working parameters, it is observed that for films grown at 200 mA, 10 mTorr in the poisoned mode, the XRD diffractograms only exhibits reflections from the low-temperature stable monoclinic (m) phase. To the contrary, while working inside the transition zone i.e. by growing sub-stoichiometric zirconium oxide thin films as demonstrated by careful elemental characterization, the film phase is dramatically modified and only the c reflections are observed. Theoretical calculations at the Density Functional Theory level are in remarkable agreement with the experimental data, hence highlighting that the incorporation of oxygen vacancies is the sole responsible mechanism for the stabilization of the c-phase. It is also observed that any deviation from the optimized working conditions i.e. change in discharge current or pressure leads to the change in film phase constitution. Thermal annealing analysis performed in air and N_2 shows the oxygen vacancy stabilized zirconia films are stable up-to 750 °C. Above 750 °C, the mechanical stress, generated in the film due to the mismatch of the thermal expansion coefficients of both the zirconia film and the substrate, apparently surpasses a critical value and leads to the appearance of m-phase.

In conclusion, c-phase of zirconia can be stabilized at room temperature (up to 750 °C) by solely incorporating oxygen vacancies in the zirconia lattice. However, increasing the energy flux during film growth or the mechanical stress may induce the transformation of the oxygen vacancy stabilized cubic phase of zirconia into the m-phase.

2:40pm **SS+AS-TuA2 W-oxide on Ag(100): a Flexible Decoupled 2-D Oxide Layer***, T. Obermüller, S. Surnev, **Falko P. Netzer**,* Karl-Franzens University, Austria

Two-dimensional (2-D) transition metal oxide layers have attracted significant interest during the past decade due to their novel emergent properties and high potential for nanotechnology applications [1,2]. For practical reasons 2-D oxide layers are usually supported on metal surfaces. This leads to a coupling of the oxide overlayer to the metal substrate, thus creating a hybrid system with properties largely determined by the oxide-metal interface. Here, we report the formation of a 2-D W-oxide layer on a Ag(100) surface, where the oxide appears to be essentially *decoupled* from the substrate. The W-oxide has been prepared by vapor phase deposition of $(WO_3)_3$ clusters at 500°C substrate temperature. The WO_x grows as a well-ordered incommensurate 2-D wetting layer in large domains with variable orientation with respect to the substrate. This gives rise to a variety of oxide domains with different azimuthal orientation, which can easily be recognized in the STM by their different Moiré patterns. The overlayer lattice can be imaged with atomic resolution in the STM and analyzed using the Moiré formula, from which the square overlayer lattice constant can be accurately evaluated to a = 3.72 Å; this is close to the respective WO_3 bulk lattice constant. AES and XPS spectra indicate an overlayer stoichiometry close to WO_3, but the W 4f binding energy suggests a lower oxidation state than W^{6+}. A structure model in terms of a 2-D WO_x sheet is discussed. It is conjectured that this WO_x sheet on Ag(100) behaves essentially like an isolated 2-D oxide layer.

[1] G. Pacchioni, *Two-dimensional oxides: multifunctional materials for advanced technologies.* Chem. Eur. J. 18(2012) 10144

[2] *Oxide materials at the two-dimensional limit.* F.P. Netzer, A. Fortunelli, Eds. (Springer Series in Materials Science, April 2016)

3:00pm **SS+AS-TuA3 Growth and Termination of a Rutile IrO2(100) Layer on Ir(111)***, **Rahul Rai**, T. Li, Z. Liang,* University of Florida, Gainesville*; M. Kim, A. Asthagiri,* Ohio State University*; J.F. Weaver,* University of Florida, Gainesville

Iridium oxide is an effective catalyst for promoting electrochemical water splitting and is a promising material for effecting other chemical transformations as well. In this talk, I will discuss our recent investigations of the growth and termination of a crystalline $IrO_2(100)$ film that develops during the oxidation of Ir(111) by gaseous O-atoms. We characterized the oxidation of Ir(111) using temperature programmed desorption (TPD), low energy electron diffraction (LEED), low energy ion scattering spectroscopy (LEISS) and density functional theory (DFT) calculations. We find that a well-ordered surface oxide with (√3 × √3)R30° periodicity relative to Ir(111) develops as the oxygen coverage increases to 1.4 ML (monolayer). Continued oxidation produces a rutile $IrO_2(100)$ layer that reaches a kinetic saturation, under the conditions employed, after the growth of about four atomic layers and decomposes during TPD to yield a sharp O_2 desorption peak at ~770 K. We assert that favorable lattice matching at the $IrO_2(100)/Ir(111)$ interface is responsible for the preferential growth of the $IrO_2(100)$ facet during the initial oxidation of Ir(111), as LEED reveals the formation of a well-defined (6 × 1) coincidence structure. TPD experiments show that CO and H_2O probe molecules bind weakly on the $IrO_2(100)$ surface, and LEISS measurements reveal that the oxide surface is strongly enriched in O-atoms. These characteristics provide evidence that the rutile $IrO_2(100)$ layer is oxygen-terminated, and therefore lacks reactive Ir atoms that can strongly bind molecular adsorbates. Finally, I will discuss our DFT predictions of the stability of so-called on-top and bridging oxygen atoms on rutile IrO_2 and RuO_2 surfaces. The DFT results support the conclusion that $IrO_2(100)$ is oxygen-terminated at the growth temperatures that we employed (< 650 K), and further reveal that on-top oxygen atoms significantly destabilize bridging oxygen atoms on the rutile (100) surfaces; such destabilization is less pronounced on the (110) surfaces. This destabilization may explain our observation that the desorption of on-top oxygen atoms and complete decomposition of the $IrO_2(100)$ film occur over a similar range of temperatures during TPD. Our findings have implications for understanding the generation of rutile IrO_2 layers for model surface chemistry studies.

3:20pm **SS+AS-TuA4 Vibrational Spectroscopy of Iron Oxide Nanostructures and Thin Films Supported on Graphite***, **Joel Langford**, F. Rosner, J.Y. Kwon, J.C. Hemminger,* University of California Irvine

Iron oxide nanostructures supported on highly oriented pyrolytic graphite have been investigated with high resolution electron energy loss spectroscopy (HREELS) and Auger electron spectroscopy (AES). The average O:Fe ratio, as measured by AES, can be increased or decreased by annealing in an oxygen background of $1x10^{-7}$ Torr or *in vacuo*, respectively. Depending on annealing temperature, and oxygen exposure, the O:Fe ratio can range from near metallic to hematite (Fe_2O_3) stoichiometry. Regardless of stoichiometry, no iron oxide vibrational modes were observed in the specular HREELS spectra. Only the collective free charge carrier excitation of the graphite substrate was observed. The absence of iron oxide modes in specular HREELS is due to an electrostatic screening from the surface dipole generated by the collective graphite excitation. This screening effect is supported by calculations of the electron energy loss function for a thin iron oxide film supported on graphite. Off specular HREELS shows that the graphite phonon dispersion is unperturbed by the presence of iron oxide nanostructures. Thus, there is minimal interaction between the graphite substrate and the supported iron oxide nanostructures. HREELS spectra of water and carbon monoxide adsorbed on iron oxide nanostructures show hindered vibrational modes. The intensity of the hindered mode is high when compared to the intramolecular modes and the elastic peak. The intensity enhancement is due to a resonance effect between the hindered mode and a longitudinal phonon mode of the nanoparticle i.e. a substrate Fermi resonance. A more descriptive interpretation of this resonant enhancement and finite relaxation lifetime based off perturbation theory will be discussed.

4:20pm **SS+AS-TuA7 Electron Transfer Processes on Single Crsystalline Alkaline Earth Metal Oxide Films***, **Thomas Risse**,* Freie Universität Berlin, Germany **INVITED**

Charge transfer processes are central ingredients to understand the chemical and physical properties of matter in general and on surfaces in particular. These processes may be classified into transient charge transfer states as created e.g. after photo excitation and processes, which create metastable charge transfer products such as molecular radicals. The Presentation will be restrict to the discussion of spontaneous charge transfer processes and will among other techniques discuss results obtained by electron paramagnetic resonance (EPR) spectroscopy to characterize paramagnetic species.

We will focus on results obtained on single crystalline, epitaxial MgO(001) film and show how film thickness, defects as well as dopants in the film are involved in charge transfer processes both between intrinsic species within the MgO as well as adsorbates such as molecular oxygen or metal atoms.

5:00pm **SS+AS-TuA9 Tungsten Trioxide Monolayer on Pd(100)***, N. Doudin, M. Blatnik,* Karl-Franzens University, Austria*; D. Kuhness,* Karl-Franzens University, Germany*; A. Fortunelli,* CNR-ICCOM & IPCF Pisa, Italy*; F.P. Netzer, **Svetlozar Surnev**,* Karl-Franzens University, Austria

Tungsten trioxide (WO_3) is a key material in several applications including smart windows technology, photo-electrochemical water splitting, gas sensors and heterogeneous catalysis. In particular, tungsten oxides are important acid-base and redox catalysts, and they show excellent activity for many catalytic reactions, such as alcohol dehydrogenation, alkane hydrogenation and metathesis [1]. WO_3 has been produced in single crystal form or as supported thin films with the bulk crystal structure. Recently, the formation of an ordered two-dimensional (2D) tungsten oxide layer on Pt(111) has been reported, where W atoms show a mixture of 5+ and 6+ oxidation states [2].

Here we report on the preparation of a well-ordered 2D WO_3 layer on a Pd(100) surface and the characterization of its geometric, electronic and vibrational structure by a combination of STM, LEED, XPS, HREELS measurements, supported by DFT calculations. The WO_3 monolayer on Pd(100) surface and features a surface network consisting of small (~ 4 nm) square-shaped domains, separated by narrow (~ 0.3 nm) trenches (Fig. 1a). The latter are identified as anti-phase domain boundaries, as evidenced by atomically-resolved STM images (see inset of Fig. 1a) and the characteristic spot splitting in the LEED pattern (Fig. 1b). The STM image shows that each domain exhibits a square surface structure with a lattice constant of 0.39 nm, which corresponds to a c(2x2) superstructure. Another important feature is the presence of few dark depressions inside the domains, which we attribute to missing terminal O atoms (see model in Fig. 1d), in corroboration with HREELS results and high-resolution W 4f core-level spectra (Fig. 1c). The latter consist of three $4f_{7/2}$ - $4f_{5/2}$ doublet components, due to W atoms at different surface locations: within the defect-free areas (major component at 34.4 eV), with missing terminal oxygens (minor component at 33.3 eV), and at the domain boundaries (35.2 eV). The DFT derived structure model of the WO_3 monolayer is shown in Fig. 1d and consists of a layer of O atoms adsorbed in on-top Pd positions, followed by a c(2x2) layer of W atoms, which are connected at the top to terminal O atoms via strong W=O bonds, as suggested by the HREELS results. It can be viewed in a way as a 2D analogue of a cubic $WO_3(001)$ crystal, featuring a similar lattice constant (0.39 nm vs. 0.38 nm) and polyhedral linkage, but with a modified W-O coordination sphere due to the contact with the Pd(100) surface.

[1] D. Gazzoli et al, J. Phys. Chem. B 101 (1997) 11129

[2] Z. Li, et al, J. Phys. Chem. C 115 (2011) 5773

This work has been supported by the FWF Project P26633-N20 and by the EU COST Action CM1104.

5:20pm **SS+AS-TuA10 Electron Energy Loss Study of Excess Electrons in Reducible TiO_2: Dual Behaviour or Coexistence of Trapped and Free States? Bulk or Surface Defects?***, **Remi Lazzari**, J. Li, J. Jupille,* Institut des NanoSciences de Paris, France

Stoichiometry defects play a tremendous role in the surface chemistry of titanium oxide [1,2]. Reduced rutile is indubitably a n-type semiconductor in terms of electrical transport but electron-based spectroscopies and scanning tunnelling microscopy show the existence of a defect-related gap state lying 0.8-1eV below the Fermi level [1,2]. Its nature *i.e.* surface oxygen vacancies [2,3] versus sub-surface interstitial titaniums [4] is still highly debated in the literature as well the actual (de)localisation of the associated excess electrons [4,5,6].

In our work, electron energy loss spectroscopy in low and high resolution modes was used to probe band gap state and phonon excitations in TiO_2(110) as a function of oxygen exposure at 100 and 300K. By comparing surfaces, from reduced to fully oxidized obtained by various means including electron bombardment, and by using EELS depth sensitivity in out-of-specular detection, a contribution from sub-surface defects is clearly evidenced. A method to prepare defect-free surfaces (as observed by EELS) is even proposed. Using dielectric modelling of spectra including phonons, carriers, gap state and interband transitions and multiple excitations, it was shown that “free-like” carriers characterized by their plasmon excitation coexists with band gap states. While the latter give rise to an obvious peak in the band gap, the former induce a temperature dependent broadening of the quasi-elastic peak and a sizeable screening and upward frequency shift of phonons compared to stoichiometric samples. Through data fitting, both surface and bulk carrier densities and dampings could be quantified as well their profile. A very different dynamics of the healing of the associated signals upon O_2 exposure was also observed. The implication of such findings in terms polaronic nature of excess electron will be discussed.

[1] U. Diebold, Surf. Sci. Rep. 48 (2003) 43; C. Pang *et al.*, Chem. Rev. 113 (2013) 3887

[2] C. Yim *et al.*, Phys. Rev. Lett. 104 (2010) 036806

[3] P. Kruger *et al.*, Phys. Rev. Lett 100 (2008) 055501

[4] S Wendt *et al.*, Science 320 (2008) 1755

[5] M. Setvin *et al.*, Phys. Rev. Lett. 113 (2014) 086402

[6] A. Janotti *et al.*, Phys. Stat. Solidi RRL 7 (2013) 199

6:00pm **SS+AS-TuA12 Vanadium on Anatase TiO_2***, **Stig Koust**, L. Arnarson,* iNANO, Aarhus University, Denmark*; P.G. Moses,* Haldor Topsøe Research Lab, Denmark*; I. Beinik, J.V. Lauritsen, S. Wendt,* iNANO, Aarhus University, Denmark

Tighter regulations concerning nitrogen oxides (NOx) and an increased public concern, highlighted recently by a study from ICCT [1], demonstrating that new diesel cars emit more than seven times the allowed NOx, has clearly shown the urgent need for the development of more effective catalysts for the removal of NOx. The Selective Catalytic Reduction (SCR) is widely used to reduce NOx into N_2 and H_2O in flue and exhaust gasses. This reaction is best catalyzed using a TiO_2-anatase supported sub-monolayer VOx-based catalyst.

Unfortunately, the detailed reaction mechanism(s) are still debated, and the nature of the active site is uncertain [2]. To tackle these issues, the preparation and characterization of good model catalyst model systems may provide new fundamental insights.

Here we present atomically resolved STM images of sub-monolayer vanadium (V) supported on anatase TiO_2 (101). Upon V deposition at liquid nitrogen temperature (LT), the surface is covered with small isolated V clusters, distributed homogeneously on the terraces. Further characterization with XPS revealed the oxidation state of V being 2+, indicating a preferred binding between V clusters and surface oxygen atoms. This conclusion is further supported by the observed reduction of the titanium surface atoms.

Surprisingly, our STM studies revealed an embedding of vanadium into the near-surface region already at room temperature (RT). A significant decrease in the density of V clusters is observed after annealing at RT and new features in the STM images appeared, which we assign to monomeric V atoms at regular titanium lattice sites, substituting the surface titanium. This change in the surface is accompanied by a shift of the V2p XPS feature to higher binding energy, revealing the oxidation of the vanadium to be 3+/4+ as compared to only 2+ upon LT deposition. The V2p area is unaltered after annealing at RT, suggesting no loss of V due to re-evaporation or migration into the bulk. Our DFT calculations confirm the substitution of vanadium with surface titanium atoms.

Additionally we present STM and XPS studies of vanadia (V_2O_5) depositedon a-TiO_2 (101) in comparison to metallic vanadium on the same surface. Vanadia displays weaker interaction with the surface compared to vanadium and we observe diffusion in to the sub-surface for vanadia after annealing at ~700K, however subsequent oxidation pulls vanadia back out to the surface.

1. Vicente, B., et al. *REAL-WORLD EXHAUST EMISSIONS FROM MODERN DIESEL CARS* . 2014.

2. Busca, G., et al., Applied Catalysis B: Environmental, 1998. (1–2): p. 1-36.

Surface Science
Room 104D - Session SS+HC-TuA
Photocatalysis and Photochemistry at Surfaces

Moderator: Arthur Utz, Tufts University

2:20pm **SS+HC-TuA1 Investigations of Surface Chemistry for Pyridine-catalyzed CO_2 Reduction on GaP***, C.X. Kronawitter, **Bruce Koel**,* Princeton University

The surface chemistry of N-containing heteroaromatics, molecular co-catalysts that enable the selective electrochemical reduction of CO_2 to fuels, is discussed. The presented experimental results focus on elucidating the role of the electrode surface in CO_2 reduction reactions that are co-catalyzed by pyridine. For this catalysis, exceptionally high selectivity for reduced fuels has been reported when the reaction occurs at the surface a GaP photocathode. For this reason, experimental emphasis is placed on assessing preferential adsorption sites and bonding interactions of adsorbates on surfaces of GaP. A surface science approach is used, whereby ultra-high vacuum conditions facilitate the fabrication of highly characterizable electrode-adsorbate systems. The use of single crystal surfaces permits analysis of surface chemistry independent of complicating factors such as grain boundaries and morphology. Surface-sensitive core-level and vibrational spectroscopy techniques, including high-resolution X-ray photoelectron spectroscopy, synchrotron-based photoemission, and high-resolution electron energy loss spectroscopy, are used to probe adsorbate-substrate and adsorbate-adsorbate interactions for pyridine, water, hydrogen, and carbon dioxide on GaP. Scanning tunneling microscopy was used to obtain molecular orbital-resolved images of adsorbed molecules. Conclusions from experimental results on these model systems are supported by calculations using density functional theory. This work assists in generating a molecular-level understanding of the heterogeneous processes important to the reaction mechanisms involved in the efficient photoelectrocatalytic generation of carbon-containing fuels with high energy densities.

2:40pm **SS+HC-TuA2 Photoreactivity of Benzoate Monolayers on TiO_2: Comparison of Anatase (001) and Rutile (110)***, **Erik Skibinski**, W.J.I. DeBenedetti, A. Song, A. Ortoll-Bloch, M.A. Hines,* Cornell University

The photoreactivity of organic self-assembled monolayers (SAMs) on TiO_2 surfaces is of considerable importance to applications such as dye-sensitized solar cells and photocatalytic environmental remediation. Despite extensive research, there remains little information about the reactivity of well characterized TiO_2 surfaces under ambient conditions. Here, we study the surface structure and photoreactivity of near-ideal benzoate monolayers prepared from dilute aqueous solutions and reacted at atmospheric pressure on anatase (001) and rutile (110) surfaces using scanning tunneling microscopy, infrared and x-ray photoelectron spectroscopies, and density functional theory.

We show that self-assembled monolayers of benzoate, an analogue of the organic linkage used in dye-sensitized solar cells, undergo rapid photodecomposition on both rutile (110) and anatase (001) under ultraviolet illumination in ambient and oxygen-rich conditions. Interestingly, while the two surfaces have similar, although not identical, reactivities, they differ in their reaction products, with the anatase polymorph producing a surface-bound ketene.

3:00pm **SS+HC-TuA3 Light-driven H_2 Generation using Multicomponent Semiconductor-metal Colloidal Nanorod Heterostructures***, **Tianquan Lian**,* Emory University **INVITED**

Quantum confined semiconductor nanocrystals have been widely investigated as light harvesting and charge separation components in photovoltaic and photocatalytic devices. The efficiency of these semiconductor nanocrystal-based devices depends on many processes, including light harvesting, carrier relaxation, charge separation and charge recombination. The competition between these processes determines the overall solar energy conversion (solar to electricity or fuel) efficiency. Compared with single component quantum dots (QDs), semiconductor nanoheterostructures, combining two or more materials, offer additional opportunities to control their charge separation properties by tailoring their compositions and dimensions through relative alignment of conduction and valence bands. Further integration of catalysts (heterogeneous or homogeneous) to these materials form multifunctional nanoheterostructures. Using CdSe/CdS/Pt, dot-in-rod nanorods(NRs) with Pt tips, as a model system, we are examining the mechanism of long-lived charge separation and H_2 generation in the presence of sacrificial electron donor. The rates of electron transfer, hole transfer and charge recombination are directly monitored by transient absorption and time-resolved fluorescence spectroscopy. In this talk, we will discuss the mechanism of exciton dissociation, the dependence of the rates of elementary charge transfer processes on the dimension (size and length) and band alignment in these materials, and how these rates affect the overall H2 generation efficiency.

4:20pm **SS+HC-TuA7 Quenching of Electron Transfer Reactions through Coadsorption: A Study of Oxygen Photodesorption from TiO_2(110)**, ***Greg Kimmel***, *N.G. Petrik, M. Shen, M.A. Henderson,* Pacific Northwest National Laboratory

Using temperature programmed desorption (TPD) and photon stimulated desorption (PSD), we show that coadsorbates of varying binding energies on the rutile TiO_2(110) surface exert a commensurate inhibiting influence on the hole-mediated photodesorption of adsorbed O_2. A variety of coadsorbates (Ar, Kr, Xe, N_2, CO, CO_2, CH_4, N_2O, acetone, methanol or water) were shown to quench O_2 photoactivity, with the extent correlating with the coadsorbate's gas phase basicity, which in turn determines the strength of the coadsorbate-Ti^{4+} bond. Coadsorbed rare gases inhibited the photodesorption of O_2 by ~10-25%, whereas strongly bound species (water, methanol and acetone) nearly completely inhibited O_2 PSD. We suggest that coadsorption of these molecules inhibit the arrival probability of holes to the surface. Band bending effects, which vary with the extent of charge transfer between the coadsorbate and the TiO_2(110) surface, are not expected to be significant in the cases of the rare gases and physisorbed species. These results indicate that neutral coadsorbates can exert a significant influence on charge transfer events by altering the interfacial dipole in the vicinity of the target molecule.

4:40pm **SS+HC-TuA8 Different Effects of Oxygen Adsorption on the Band Bending of TiO_2 Nanoparticles Studied by Photoluminescence Spectroscopy**, ***Shiliang Ma***, *M. Reish, Z. Zhang, I. Harrison, J.T. Yates, Jr.,* University of Virginia

By employing photoluminescence (PL) spectroscopy, it was found that oxygen adsorption on powdered TiO_2 changes the band bending of anatase in different ways. On the one hand, oxygen exposure leads to molecular chemisorption of oxygen molecules, which take up negative charge, but can be reversibly removed by ultraviolet photodesorption from the TiO_2 surface. Molecular chemisorption of oxygen molecules increases the upward band bending of TiO_2 and decreases the PL emission. On the one hand, oxygen can adsorb through irreversible reaction with defects, which occurs through an intermediate state of molecularly chemisorption, reducing the intrinsic upward band bending at the TiO_2 surface resulting in PL emission increase. Since band bending plays an important role in charge carrier migration to the surface, this finding that oxygen adsorption can have two different effects on the band bending of TiO_2 provides a new perspective on how oxygen and oxygen vacancies may modulate photocatalytic reaction efficiencies.

5:00pm **SS+HC-TuA9 Imaging Photodecomposition of Trimethyl Acetic Acid on Cross-linked (1 × 2) Rutile TiO_2(110)**, *Y. Xia, K. Zhu,* ***Zhenrong Zhang***, *K.T. Park,* Baylor University

Photoreactivity of reduced TiO_2 is important in photocatalytic applications. Cross-linked (1 × 2) rutile TiO_2(110) has been extensively studied, yet the exact atomistic model remains a point of contention. Employing a carboxylic acid as a probing molecule, we studied the structure of cross-linked (1 × 2) TiO_2(110) through the interaction of trimethyl acetic acid (TMAA) with various sites on the surfaces using *in situ* scanning tunneling microscopy (STM). We compared three specific atomistic models for (1 × 2) reconstructed TiO_2(110), Ti_2O_3, Ti_2O, and Ti_3O_6. The adsorption of TMAA on strands at room temperature strongly supports the Ti_2O model for cross-linked (1 × 2) reconstructed TiO_2(110). Photodecomposition of TMAA shows the dependence on the initial TMA coverage and O_2 pressure.

5:20pm **SS+HC-TuA10 Non-Fullerene Acceptors for Organic Photovoltaics: PTCDA versus C_{60}**, ***Steven Robey***, National Institute of Standards and Technology

Extensive development of new polymer and small molecule donors has helped produce a steady increase in the efficiency of organic photovoltaic (OPV) devices. However, OPV technology would benefit from the introduction of non-fullerene acceptors. Unfortunately, efforts to replace fullerenes have typically led to significantly reduced efficiencies. A number of possible explanations for reduced efficiencies with non-fullerene acceptors compared to fullerene acceptors have been suggested, including the formation of unfavorable morphologies in non-fullerene systems and/or favorable excitation/carrier delocalization in fullerenes. In addition, enhanced exciton dissociation associated with fundamental characteristics of the fullerene molecular electronic states has also been suggested. We employed time-resolved two-photon photoemission (TR-2PPE) to directly compare exciton dissociation at interfaces between zinc phthalocyanine (ZnPc) interfaces and the non-fullerene acceptor, perylene tetracarboxylic dianhydride (PTCDA) versus dissociation measured at the analogous interface with C_{60}, and thus help discriminate between these potential explanations. Exciton dissociation rates are comparable for phthalocyanine interfaces with both acceptors, allowing us to suggest a hierarchy for effects influencing higher efficiencies with fullerene acceptors.

5:40pm **SS+HC-TuA11 Use of Photoluminescence to Monitor Surface Chemistry of Metal Oxide Nanoparticles**, *S. Kim, D. Somaratne,* ***James Whitten***, University of Massachusetts Lowell

Many metal oxides nanoparticles are photoluminescent upon irradiation with ultraviolet light, with visible emission arising from surface states and surface defects. Because of the sensitivity of the surface to adsorption and electron transfer to and from even weakly adsorbed molecules, photoluminescece (PL) is proving to be a convenient method of monitoring chemisorption and physisorption. Experimental and theoretical results are presented related to adsorption of various gases and organic vapors on zinc oxide, zirconium oxide, and titanium dioxide nanoparticles toward the goal of correlating adsorption to PL changes. X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and Raman spectroscopy measurements have been performed on metal oxide nanoparticles and single crystals to investigate whether chemisorption occurs at room temperature and the details of adsorbate bonding. These results are combined with density functional theory (DFT) calculations to understand how adsorption influences the PL changes. In addition to atmospheric gases, examples of adsorbates that have been examined include ammonia, methanethiol, methanol, benzene, and pyridine. This research provides a convenient method of monitoring adsorption and lays the foundation for optochemical sensing, in which metal oxides may serve as a new type of gas sensor.

6:00pm **SS+HC-TuA12 Exploring Pd Adsorption, Diffusion, Permeation, and Nucleation on Bilayer SiO_2/Ru as a Function of Hydroxylation and Precursor Environment: From UHV to Catalyst Preparation**, ***William Kaden***, University of Central Florida

The hydroxylation-dependent permeability of bilayer SiO_2 supported on Ru(0001) was investigated by XPS and TDS studies in a temperature range of 100 K to 600 K. For this, the thermal behavior of Pd evaporated at 100 K, which results in surface and sub-surface (Ru-supported) binding arrangements, was examined relative to the extent of pre-hydroxylation. Samples containing only defect-mediated hydroxyls showed no effect on Pd diffusion through the film at low temperature. If, instead, the concentration of strongly bound hydroxyl groups and associated weakly bound water molecules was enriched by an electron-assisted hydroxylation procedure, the probability for Pd diffusion through the film is decreased via a pore-blocking mechanism. Above room temperature, all samples showed similar behavior, reflective of particle nucleation above the film and eventual agglomeration with any metal atoms initially binding beneath the film. When depositing Pd onto the same SiO_2/Ru model support via adsorption of $[Pd(NH_3)_4]Cl_2$ from alkaline (pH 12) precursor solution, we observe notably different adsorption and nucleation mechanisms. The resultant Pd adsorption complexes follow established decomposition pathways to produce model catalyst systems compatible with those created exclusively within UHV despite lacking the ability to penetrate the film due to the increased size of the initial Pd precursor groups.

Surface Science
Room Hall D - Session SS-TuP
Surface Science Poster Session

SS-TuP1 Adsorption and Decomposition Properties of Dimethyl Trisulfide Over Au(111)*, **Isao Nakamura**, National Institute of Advanced Industrial Science and Technology (AIST), Japan; M. Tokunaga,* Kyushu University, Japan*; T. Fujitani,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

It is known that dimethyl trisulfide (DMTS) is mainly responsible for an off-flavor that develops during the storage of Japanese sake. Recently, we found that the supported gold catalysts are effective for the adsorption and removal of DMTS. In this study, in order to clarify the reaction properties of DMTS over gold, we investigated the adsorption and decomposition of DMTS using the Au(111) single-crystal surface.

First, we examined the influence of the exposure temperature on the adsorption properties of DMTS. X-ray photoelectron spectroscopy (XPS) results indicated that DMTS is dissociatively adsorbed as CH_3S and CH_3SS species at 100–300 K. Furthermore, both the dissociative adsorption rate and the saturation coverage were the same regardless of the exposure temperature.

In contrast, the thermal decomposition properties of CH_3S and CH_3SS strongly depended on their formation temperatures. On the Au(111) surface formed at 100 K, the CH_3S was shown to be associatively desorbed as dimethyl disulfide (DMDS), and the production of ethane and atomic sulfur by the cleavage of C–S bond in CH_3SS were confirmed from temperature-programmed desorption and XPS measurements. Thus, CH_3S and CH_3SS reacted individually. On the other hand, the reaction of CH_3S with CH_3SS to produce DMDS and atomic sulfur was also confirmed for the surface at 150 K. At 200 K or 300 K, only the reaction of CH_3S with CH_3SS was observed. We consider that the difference in the decomposition reaction is due to that the adsorption structure of CH_3S and CH_3SS species on Au(111) changes by their formation temperatures. That is, the CH_3S and CH_3SS species are present in separate islands each other at 100 K, whereas the adsorption structure of CH_3S and CH_3SS becomes random with rising their formation temperatures.

SS-TuP2 Spectroscopically Monitoring the Surface and Crystallinity of Titania Nanopowders Treated with Hydrogen Peroxide: an Endeavor in Simplifying the Atomic Picture of Complex Substrates*, **Maria Kipreos**, M. Foster,* University of Massachusetts, Boston

Metal oxide substrates are often riddled with defect sites, imperfections in metal-oxide atomic arrangements. One such defect is an oxygen vacancy at the surface. Commonly, the substrate is exposed to O_2 to reestablish the proper metal-oxygen coordination. Much like O_2, hydrogen peroxide may be used to oxidize the surface of metal oxide nanopowders, such as titania (TiO_2), as well as drive off impurities remaining and or derived from the synthesis of these materials, to establish a more pristine surface. Various commercially available nanosized rutile and anatase structured titania nanopowders are treated with hydrogen peroxide and any changes in crystallinity are monitored using a confocal Raman microscope as well as powder X-ray Diffraction. In situ DRIFTS coupled with a high temperature reaction chamber is used to assess any changes in the substrate upon treatment, including evolving water and hydroxyl features on the surface and the disappearance of impurities, both as the pretreatment conditions change and as a function of substrate temperature.

SS-TuP3 Efficacy of Ar^+ CIRD Removal of Adsorbed O from Rh(111)*, **Marie Turano**, R.G. Farber, D.R. Killelea,* Loyola University Chicago

Subsurface oxygen (O_{sub}) on Rh(111) is formed via gas-phase deposition of atomic oxygen (AO). Total O coverages of over 3 ML equivalence are possible, and results in an oxygen saturated surface and O_{sub}. In order to study the geometric and electronic effects of O_{sub} on a surface alone requires a technique to remove the adsorbed oxygen (O_{ad}) while retaining O_{sub} and minimizing damage to the metal surface. Here, we present results from our development of collision-induced recombinative desorption (CIRD) of O_{ad} from Rh(111) using Ar^+ ions from a commercial sputter gun. We show that with proper selection of the Ar^+ energy and electronic bias of the metal surface, O_{ad} can be removed leaving behind a cleared Rh(111) surface still charged with O_{sub}. We characterized the surface with a combination of structural probes (LEED, STM) and temperature programmed desorption to quantify total oxygen and Auger electron spectroscopy for the surface coverage.

SS-TuP4 Adsorption and Oxidation of n–Butane on the Stoichiometric $RuO_2(110)$ Surface*, **Tao Li**, R. Rai, Z. Liang,* University of Florida, Gainesville*; M. Kim, A. Asthagiri,* Ohio State University*; J.F. Weaver,* University of Florida, Gainesville

The surface chemistry of late transition-metal (TM) oxides has drawn significant attention due to the observation and prediction of facile C-H bond cleavage of molecularly adsorbed n-alkanes at low temperatures. Previous studies have shown that PdO(101) readily promotes the dissociation of alkanes by a mechanism in which adsorbed σ-complexes serve as precursors to initial C-H bond cleavage. Density functional theory (DFT) calculations further predict that the formation and facile C-H bond activation of alkane σ-complexes should also occur on RuO_2 and IrO_2 surfaces, suggesting that the σ-complex mechanism is a common pathway for alkane activation on late TM oxides.

In this study, we investigated the adsorption and oxidation of n-butane on the stoichiometric $RuO_2(110)$ surface using temperature-programmed reaction spectroscopy (TPRS) and DFT calculations. At low coverage, molecularly adsorbed n-butane achieves a binding energy of ~100 kJ/mol on $RuO_2(110)$, consistent with a strongly bound σ-complex that forms through dative bonding interactions between the n-butane molecule and coordinatively unsaturated (cus) Ru atoms. We find that a fraction of the n-butane reacts with the RuO_2 surface during TPRS to produce CO, CO_2, and H_2O that desorb above ~400 K and present evidence that adsorbed σ-complexes serve as precursors to the initial C−H bond cleavage and ultimately the oxidation of n-butane on $RuO_2(110)$. From measurements of the product yields as a function of surface temperature we estimate that the initial reaction probability of n-butane on $RuO_2(110)$ decreases from 9% to ~4% with increasing surface temperature from 280 to 300 K and show that this temperature dependence is accurately described by a precursor-mediated mechanism. From kinetic analysis of the data we estimate a negative, apparent activation energy of −35.1 kJ/mol for n-butane dissociation on $RuO_2(110)$ and an apparent reaction prefactor of 6×10^{-8}. The low value of the apparent reaction prefactor suggests that motions of the adsorbed n-butane precursor are highly restricted on the $RuO_2(110)$ surface. DFT calculations confirm that n-butane forms strongly bound σ-complexes on $RuO_2(110)$ and predict that C−H bond cleavage is strongly favored energetically. The n-butane binding energies and energy barrier for C−H bond cleavage predicted by DFT agree quantitatively with our experimental estimates. Our results support the idea that the σ-complex mechanism is a common pathway for alkane activation on late TM oxide surfaces that expose pairs of cus metal and oxygen atoms.

SS-TuP5 Step-type Dependence of Water Desorption from Single-Crystalline Ag Surfaces*, **Sabine Auras**,* Leiden University, Netherlands*; J. Janlamool,* Chulalongkorn University, Bangkok

Many heterogeneously catalyzed reactions have been shown to be strongly structure dependent.[1] Catalytically active materials can feature a wide spectrum of defect densities on the same sample and may include various step types.[2] Thus, curved crystals with continuously changing average step densities provide a good alternative to flat single crystals for the investigation of surface structure dependencies.[3] In this study we use two curved Ag single crystals to exemplify the strength of this approach to studying structure dependencies. The crystals have two different apex orientations. One Ag crystal with a [111] apex contains two different step sites on either side of the center, generally referred to as the (100) and (111) or A and B step types. The step density gradually increases until at the edges of the crystal we reach 5-atom wide (111) terraces. The crystal with the [100] apex has only one step type, that resembles the B step type from the first crystal, but has adjacent (100) terraces. We study the surface structure of the clean crystals with LEED and STM and show that the surface behaves as may be expected with single-atom high steps.

Subsequently, water adsorption to the steps and their effect on the water-metal interface are investigated using spatially resolved Temperature Programmed Desorption. As Ag binds water only weakly, effects resulting from the available steps are expected to be rather small . We show how the different step types affect the desorption of water and how it would be nearly impossible to measure the effects using multiple flat Ag samples.

1. Somorjai, G.A. The structure sensitivity and insensitivity of catalytic reactions in light of the adsorbate induced dynamic restructuring of surfaces. *Catal. Lett.***1990**, *7*, 169–182.

2. Walter, A.L.; Schiller, F.; Corso, M., et al. X-ray photoemission analysis of clean and carbon monoxide-chemisorbed platinum(111) stepped surfaces using a curved crystal. *Nat. Commun.* **2015***, 6*, 8903.

3. (a) Besocke, K.; Krahl-Urban, B; Wagner, H. Dipole moments associated with edge atoms; A comparative study on stepped Pt, Au and W surfaces, *Surf. Sci.***1977**, *68*, 39–46.

(b) Hopster, H.; Ibach, H.; Comsa, G. Catalytic oxidation of carbon monoxide on stepped platinum(111) surfaces, *J. Catal.***1977**, *46*, 37–48.

(c) Pluis, B.; van der Gon, A.W.D.; Frenken, J.W.M.; van der Veen, J.F. Crystal-Face Dependence of Surface Melting, *Phys. Rev. Lett.***1987**, *59*, 2678–2681.

SS-TuP6 Topographical Changes of Liquid-Metal Alloys as a Function of Temperature*, Nelson Bello,* University of Massachusetts, Boston*; I. Tevis,* SAFI-Tech*; M. Thuo,* Iowa State University*; M. Foster,* University of Massachusetts, Boston

Gallium-indium metal alloys are remarkable materials that, at the eutectic composition, are liquid at room temperature and form a very thin (0.7 nm) passivating oxide film on the surface. This makes them valuable in the field of molecular electronics as soft conformal electrical contacts and as, potentially, self-repairing wires. For this project, EGaIn is put through a fluidic shearing process that produces 3-layered core-shell nano/micro-spherical particles composed of a chemisorbed organic outer layer on an oxide film around the liquid metal core that prevents their coalescence. We used Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) to monitor topographical changes in these particles as a function of temperature. The liquid metal has a different rate of expansion from the oxide shell, and AFM coupled with SEM are especially well-suited to monitor these changes both as a function of the rate of change of the temperature and the thickness of the oxide film. The nature of the external coating can also be tuned through exposure of the particles to strong oxidants or shearing the metal in the presence of different surfactants. The effect of the different film coatings and the expansion of the particles upon application of heat will be discussed.

SS-TuP7 Interaction of Ethylene with Partially Chlorinated $RuO_2(110)$ Surfaces*, Zhu Liang,* *T. Li, R. Rai, J.F. Weaver,* University of Florida

Partial replacement of surface oxygen atoms with chlorine atoms may provide a means for modifying the activity and selectivity of oxide surfaces toward hydrocarbon oxidation. In this study, we investigated the adsorption and oxidation of ethylene on partially chlorinated $RuO_2(110)$ surfaces using temperature programed reaction spectroscopy (TPRS) and X-ray photoelectron spectroscopy (XPS). Chlorination of the $RuO_2(110)$ surface occurs when exposing the stoichiometric surface to gaseous HCl at 700 K, where the bridging oxygen atoms are selectively replaced by chlorine atoms. The degree of chlorination is controlled by the amount of HCl gas introduced, and characterized by XPS. Compared with stoichiometric $RuO_2(110)$, we find that bridging Cl atoms weaken the binding and suppress the oxidation of ethylene, without shifting the selectivity toward partially oxidized products. We also find that on-top oxygen atoms significantly enhance the activity of both s-$RuO_2(110)$ and chlorinated $RuO_2(110)$ surfaces toward the complete oxidation of ethylene. The enhanced reactivity arises from an increase in the ethylene coverage achieved on the O-rich surfaces as well as more facile C–H bond cleavage of ethylene via H-transfer to on-top vs. bridging oxygen atoms. Our results provide evidence that ethylene molecules achieve high coverages on the O-rich surfaces by preferentially binding to stranded Ru sites located between on-top oxygen atoms, and that such configurations are responsible for the high activity of the O-rich RuO_2 and RuO_xCl_y surfaces. These findings demonstrate that the relative reactivity of on-top vs. bridging oxygen atoms plays a decisive role in determining the chemical activity of partially-chlorinated RuO_2 surfaces, and that high reactivity can be achieved on O-rich RuO_xCl_y surfaces.

SS-TuP8 Supramolecular Assemblies of Halogenated Molecules on the Si(111) $\sqrt{3}\times\sqrt{3}$-Ag and Cu(100) Surfaces*, Renjie Liu,* Lakehead University, Canada*; C. Fu, A.G. Moiseev, D.F. Perepichka,* McGill University, Canada*; M.C. Gallagher,* Lakehead University, Canada

The surface-confined assembly of two-dimensional (2-d) covalent organic frameworks (COF) has gained much attention [1]. One approach to COF formation is the adsorption of halogenated aromatic precursors onto a noble metal surfaces, followed by dehalogenation of the precursors, and subsequent covalent coupling. We have studied the adsorption of a halogenated organic molecule, 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (TIPT), on both the Cu(100) and Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surfaces by scanning tunneling microscopy (STM). Recently, we found that the Si $\sqrt{3}$–Ag surface can provides an inert, high-mobility template for the adsorption of halogenated organic molecules [2].

STM images reveal that TIPT monomers are quite mobile on the Cu(100) surface at room temperature. At low coverage, molecules readily migrate and accumulate at step edges. We observe very few supramolecular features at the surface, and these structures often decompose after repeated STM scanning. In contrast to the as deposited samples, after annealing to 420°K more robust open pore structures are observed. The structure and size of these molecular frameworks are consistent with covalent linking. We have also studied TIPT adsorption on the $\sqrt{3}$-Ag surface. The structure of these films as a function of coverage and annealing temperature will be discussed.

1. D.F.Perepichka, and F. Rosei, *Science* **323**, 216–217 (2009).

2. R. Liu et al., *Surf. Sci.* **647**, 51–54 (2016).

SS-TuP9 Synthesis and Reduction of Graphene Oxide*, Heike Geisler*, *J.M. Bachor, N.A. LaScala,* SUNY College at Oneonta

Graphite oxide was successfully synthesized from graphite powder using the modified Hummers method*. The graphite oxide was then exfoliated to yield graphene oxide which was subsequently reduced to give reduced graphene oxide. This employed two different chemical reduction methods, and one effective combination of the two. The two methods being a weaker sodium borohydride/calcium chloride catalyst and a hydrogenation through hydrogen produced from the reaction of hydrochloric acid and aluminum. This can be seen through the removal of various functional groups from our graphene oxide sample after each reduction method, as shown in FTIR spectra of each sample. While the reduction methods employed did remove a number of oxygenated functional groups on the graphene oxide sheet, we still observe the presence of hydroxyl and some carboxylic acids that persist through. We also notice the appearance of a well-defined peak at ~1600 cm^{-1} representing the conjugated system in the combined reduction method.

** W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339*

SS-TuP10 Nanomechanical Properties of Eutectic Gallium-Indium Particles by Atomic Force Microscopy*, Syeda Akhter,* University of Massachusetts, Boston*; I. Tevis,* SAFI-Tech*; M. Thuo,* Iowa State University*; M. Foster,* University of Massachusetts, Boston

Eutectic Gallium-Indium (EGaIn) alloy is a liquid metal at room temperature that, under air, forms a passivating native thin (~0.7 nm) oxide layer. This oxide layer plays an important role in the overall mechanical properties of the alloy. The metallic and physical properties of EGaIn make it effective at conducting, and dissipating, heat away from temperature sensitive components. Being a deformable liquid metal, EGaIn is consistently electrically conductive even when a supporting polymeric channel is excessively stretched. EGaIn particles, with a liquid core and a thin oxide shell, are created with diameters that range from 6.4 nm to >10 µm using fluidic shearing. The mechanical properties, such as the flexibility of the oxide shell, especially on nano- and micro-particles, are unknown. Atomic Force Microscopy, however, is a versatile instrument for imaging surface topography as well as for characterizing material properties, such as elasticity and film thickness at the micro- and nanoscale via force-distance curves (F-D curves). F-D curves are the result of interactions, upon contact, between an AFM tip and the surface of the sample due to the elastic force of the cantilever and values can be measured with resolutions up to pico-Newtons. This poster describes our studies on mechanical properties of EGaIn thin film and particles of various sizes via AFM F-D curves.

SS-TuP11 Reactivity of CO_2 at Single-site Vanadium in Metal-Organic Coordination Networks at Surfaces, *C. Tempas, B. Cook,* Indiana University*;* ***David Wisman,*** Indiana University; NAVSEA Crane*; T. Morris, A. Polezhaev, D. Skomski, K. Smith, K. Caulton, S.L. Tait,* Indiana University

Driven by growing concern of the effect of greenhouse gases on the environment, CO_2 chemistry has become an increasingly active area of research. The interaction of CO_2 with metal-organic complexes offers opportunities for CO_2 recycling, but those chemistries have not been developed in surface catalysts, which could offer much higher efficiency. We have developed a prototypical metal-organic network that shows chemical activity toward CO_2 by co-depositing bis-pyridinyltetrazine (DPTZ) and metallic vanadium on a Au(100) surface. These organize at room temperature into highly-ordered one-dimensional metal-organic chains. We characterized the assembly by high-resolution scanning tunneling microscopy. The chains align in specific orientations relative to the underlying gold surface due to their interaction with the gold. The assembly occurs by a redox-active self-assembly process, in which the vanadium oxidizes to the +2 state and there is corresponding reduction of the ligand, as observed by X-ray photoelectron spectroscopy. Exposure to CO_2 gas leads to a shift in the vanadium oxidation state to +4; the shift is gradual with increasing CO_2 exposure. The 1D chains generally remain intact during the CO_2 exposure, but become somewhat less ordered with increasing exposure time. Following gas exposure, the surface was annealed at various temperatures. At annealing temperatures of 250 °C and greater we observe desorption of the ligand and the shift of vanadium back to the +2 state, indicating a residual vanadium-oxo species on the surface. Developing single-site metal center surfaces systems with chemical activity toward CO_2 may lead to the development of new methods for CO_2 capture and recycling, as well as providing more general insight into the development of next-generation catalysts.

SS-TuP12 CO_2 Optical Phonons for Constraining Mixing in Interstellar Ices*, **Ilsa Cooke**, University of Virginia; K.I. Öberg,* Harvard University

CO_2 is an important ice species in interstellar environments, often the second most abundant ice after H_2O. Astronomical infrared spectra of interstellar objects have revealed abundant CO_2 in a variety of protostellar environments as well as in cold dark clouds. The CO_2 v_2 band has been used as a tracer of thermal processing due to its dependence on the ice temperature and local environment; however, there are still uncertainties involved in fitting the laboratory v_2 band to astronomical spectra. We report laboratory spectra of the CO_2 longitudinal optical (LO) phonon mode for a series of CO_2 ices at low temperature and for ice mixtures with polar (H_2O) and non-polar (CO, O_2) components. We show that the LO phonon mode is particularly sensitive to the mixing ratio of various ice components of astronomical interest. These spectra may be useful in constraining the bulk environment of CO_2 in astronomical ices as well as for tracing ice mixing in laboratory experiments.

SS-TuP17 Probe the Degradation Mechanism of Hybrid Perovskite by *In Situ* DRIFTs*, Q. Peng, X. Yu, **Amanda Volk**,* University of Alabama

Methylammonium Lead Iodide Perovskite ($MAPbI_3$) is a promising photoelectronic material for photovoltaics and LEDs. However, the stability of $MAPbI_3$ under the external application environments is a big concern. The underlying mechanism of decomposition of $MAPbI_3$ is not well understood yet. In this poster, we will use *in-situ* Diffuse reflectance infrared fourier transform spectroscopy for the first time to understand the surface reaction mechanism in the decomposition of $MAPbI_3$ in various related applications environments. With the unique setup and high-surface-area configuration, our results showed that the degradation rate is strongly affected by the temperature and chemical composition of the application environments. The degradation mechanism of $MAPbI_3$ changes with the application environments. Our results provide a fresh view of the degradation pathways of $MAPbI_3$ and will help optimize the synthesis of $MAPbI_3$ and provide potential solutions for stabilizing $MAPbI_3$.

SS-TuP19 Interaction of Atomic Oxygen with Ag(111) and Ag(110) Surfaces: Oxygen Adsorption at Surface versus Subsurface*, **Sara Isbill**, S. Roy,* University of Tennessee, Knoxville

While transition metals are commonly used to catalyze the oxidation of small organic compounds, the mechanisms of these 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 by silver surfaces, several aspects of the catalysis, particularly the different ways in which oxygen interacts with the silver surface have yet to be elucidated. This understanding is critical to determine the catalytically active oxygen-silver species that interacts with the reactants. It is also important to know how these active species change with reaction conditions, such as surface structure, surface temperature, and oxygen coverage, such that the conditions can be tuned to design the most effective catalysts. In the present study, density functional theory (DFT) was used to probe atomic-oxygen adsorption at the surface and subsurface of Ag(111) and Ag(110) surfaces. The main goal was to investigate the competition between surface and subsurface oxygen at different oxygen coverages, and study their participation in oxidation catalysis by silver surfaces. On the Ag(111) surface, it was found that adsorption energies for all surface and subsurface sites decreased with coverage; however, surface adsorption was compromised much more than subsurface adsorption. This difference causes a flip in preference from surface adsorption at low coverages to subsurface adsorption at high coverages. Calculated potential energy curves of oxygen moving from surface to subsurface on Ag(111) and Ag(110) show a complex interplay between adsorption energies and energy barriers that is sensitive to monolayer coverage. Results provide valuable insight into the competition between surface adsorption and subsurface adsorption of oxygen on the silver surface, the role of subsurface oxygen in catalysis by the silver surface, and the importance of charge transfer in the adsorption and dynamics of oxygen on the silver surface.

SS-TuP20 Isotope Fractionation Effect in Secondary Ions Mass Spectroscopy Analysis for Boron Quantification*, **Yibin Zhang**,* GLOBALFOUNDRIES U.S. Inc.

Secondary Ion Mass spectroscopy (SIMS) analysis is heavily used in semiconductor, lighting/LED, solar/PV industries for routine manufacturing and research/development due to its versatility, fast turnaround time and excellent accuracy/precision. There are some factors that affect the accuracy of SIMS quantification. Fractionation is one of them. It is very important for isotope abundance measurement and for applying RSFs from one isotope to another. If fractionation is ignored during SIMS quantification by applying RSFs from one isotope to another, over 10% error could be introduced. Boron is a useful dopant for such semiconductors as silicon, germanium, and silicon carbide. Having one fewer valence electron than the host atom, it donates a hole resulting in p-type conductivity. Then to accurately monitor Boron concentration in semiconductor manufacturing process is very important. In this study, the Boron isotope fractionation was investigated on Cameca IMS WF, Cameca 7f, Quad SIMS. A methodology to quantify Boron was demonstrated by applying RSF from ^{10}B implanted standard to unknown sample by monitoring ^{11}B.

Applied Surface Science
Room 101B - Session AS+SS-WeM

Applications where Surface Analysis is Your Only Hope

Moderators: Jeffrey Fenton, Medtronic, Svitlana Pylypenko, Colorado School of Mines

8:00am **AS+SS-WeM1 Accurate Ion Beam Analysis of Electrolytes via Rutherford Backscattering (RBS) and Positive Ion X-ray Emission (PIXE) of Uniform Thin Solid film of Blood congealed via HemaDrop™*, Yash Pershad*,** *N.X. Herbots,* SiO2 NanoTech LLC*; C.F. Watson,* SiO2 NanoTech LLC/Arizona State University Physics Dpt*; EJ. Culbertson,* University of California at Los Angeles

Medical diagnostics needs new methods of blood analysis using mL of blood rather than the standard 7 mL to improve care. Theranos has been recently challenged about their “finger-stick method,” where blood drops are used for complete blood diagnostics, not just glucose. They only approved by the FDA for qualitative detection, rather than accurate blood composition. Motivated by these accuracy issues, along with the great need for diagnostics from microliters of blood, we use MeV Rutherford Backscattering Spectrometry (RBS) to measure elemental composition (H, C,N, O, K, Mg, Ca, Na, Fe) in microliters of blood congealed into smooth, planar, Homogeneous Thin Solid Films (HTSF). These planar HTSF of blood are prepared with a new technology that congeal blood drops, called HemaDrop™ [1, 2] Measurements on HTSF prepared via HemaDrop™ are compared and found much more reproducible and accurate than those taken for comparison on dried blood drops, such as the so called “Dried Dlood Spot (DBS)” that can only be used in microvolume sampling for drug metabolism, not blood composition. HTSF prepared with HemaDrop™ yields reproducible elemental composition regardless of substrate used or area of analysis with < 6% sampling error. Ion damage from RBS is accounted for via the 0-dose intercept damage curve method, which graphs RBS yield of elements detected, as a function of analysis dose, using several sequential cumulative spectra. Positive Ion X-ray Emission (PIXE) is used to verify the reproducibility and accuracy of RBS. RBS and PIXE analysis on HTSF prepared with HemaDropTM using 6 microliter of blood are found in excellent agreement within the 6% sampling error. Thus, HemaDropTM successfully creates homogeneous thin solids film from blood that can be analyzed in vacuum and can also be used for Infrared (IR) spectroscopy and Tapping Mode Atomic Force Microscopy for molecular identification and counting. HTSF enable for the first time blood analysis via vacuum-based methods. IR and TMFAM are also being investigated to add molecular identification and counting.

[1] US Patent Pending, Assignee: SiO2 NanoTech, Inventors: Herbots, N, Watson CF, Krishnan A, Pershad Y, et al (2016)

[2] Electrolytes Detection by Ion Beam Analysis, in Continuous Glucose Sensors and in Microliters of Blood using a Homogeneous Thin Solid Film of Blood, HemaDrop™. Yash Pershad, Ashley A. Mascareno, Makoyi R. Watson, Alex L. Brimhall, Nicole Herbots, Clarizza F. Watson, Abijith Krishnan, Nithin Kannan, Mark W. Mangus, Robert J. Culbertson, B. J. Wilkens, E. J. Culbertson, T. Cappello-Lee, R.A. Neglia Submitted to MRS Advances, April 2016

8:20am **AS+SS-WeM2 Surface Analysis As a Valuable Tool to Study Chemistry of Metals in Environmental Problems*, Kateryna Artyushkova,*** University of New Mexico*; J. Blake,* New Mexico Water Science Center*; L. Rodriguez-Freire, S,. Avasarala, A. Ali, A. Brearley, E. Peterson, J.M. Cerrato,* University of New Mexico

This talk will present application of X-ray Photoelectron Spectroscopy to understand the role of chemistry of metals in several environmental problems. In the first study, the chemical interactions of U and co-occurring metals in abandoned mine wastes in a Native American community in northeastern Arizona were investigated using spectroscopy, microscopy and aqueous chemistry. Elevated concentrations of metals are of concern due to human exposure pathways and exposure of livestock currently ingesting water in the area. This study contributes to understanding the occurrence and mobility of metals in communities located close to abandoned mine waste sites. Elevated U (6,614 mg/kg), V (15,814 mg/kg), and As (40 mg/kg) concentrations were detected in mine waste solids. The power of XPS in specific identification of the chemical states of these elements as U (VI), As (-I and III) and Fe (II, III) will be presented.

In the second study, the goal is to investigate the effect of metals associated with wildfire ash from wood collected from the Valles Caldera National Preserve, Jemez Mountains, New Mexico on water chemistry. Metals and other constituents associated with wildfire ash can be transported by storm event runoff and negatively affect water quality in streams and rivers. Microscopy and spectroscopy analyses were conducted to determine the chemical composition of ash. Metal-bearing carbonate and oxide phases were detected through X-ray spectroscopy analyses.

Finally, we integrated spectroscopy, microscopy, diffraction, and water chemistry to investigate the presence of metals in water and sediment samples collected 13 days after the Gold King Mine spill (occurred on August 5, 2015). Spectroscopy, microscopy, and XRD analyses suggest that Pb, Cu, and Zn are associated with metal-bearing jarosite ($KFe^{3+}{}_3(OH)_6(SO_4)_2$) and other minerals (e.g. clays, Fe-oxides and oxyhydroxides) identified in sediments from Cement Creek, CO. The presence of sulfates and phosphates, Fe as 75% Fe^{2+} and 25% Fe^{3+}, and 100% Pb^{2+} in the near surface region of these sediments was detectedby XPS analyses.

Additionally, phosphates and nitrogen species were found with XPS in the sediments from Farmington, NM, downstream the Animas River. The interaction of these metal-bearing minerals with biogeochemical processes occurring downstream could cause metal mobilization into the water.

8:40am **AS+SS-WeM3 Surface Analysis Techniques – Hope Springs Eternal*, John Newman,*** *S.R. Bryan, D.M. Carr, G.L. Fisher, J.S. Hammond, J.E. Mann,* Physical Electronics USA*; T. Miyayama,* ULVAC-PHI, Japan*; J.F. Moulder, D. Paul,* Physical Electronics USA*; R. Inoue,* ULVAC-PHI, Japan*; B. Schmidt,* Physical Electronics USA **INVITED**

In today’s technologically advanced laboratories there are many dozens of different, and very specialized, analytical techniques being used to attempt to solve problems and characterize materials. When choosing the proper technique for a particular application, the needs of the study are matched to the attributes of a particular method – its depth of analysis, detection sensitivity, analytical spot size, type of information provided, and whether or not the technique is appropriate for the sample in question. For applications where the region of interest is measured in atomic layers, surface sensitive methods such as Auger Electron Spectroscopy, X-ray Photoelectron Spectroscopy, and Time-of-Flight Secondary Ion Mass Spectrometry have always been the methods of choice and, in most cases, really the only hope for a successful analysis.

However, when we look at the relatively recent technological advances in these three methods, we find that their increased capabilities expand their usefulness to much more than the traditional types of surface experiments. For example, gas cluster beams now allow for intact organic information to be obtained from depth profiles or cross-sectioned samples; higher energy x-ray beams allow for deeper analysis depths compared to traditional XPS x-ray beams; and tandem mass spectrometry technology can provide unambiguous peak identification in TOF-SIMS. This presentation will look at applications where some of these advancements are used; exemplifying how newer technologies are making these techniques our only hope for a much wider array of studies.

9:20am **AS+SS-WeM5 What Came First? The Black Ink or the Black Ink? That Is the Question*, Robyn E. Goacher,*** *L.G. DiFonzo, K.C. Lesko,* Niagara University

Determining the order of deposition of ink markings in questioned documents (forgeries) is an important forensic task. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has received attention as a possible technique for this purpose because it is a surface sensitive technique that can provide chemical images, potentially resolving the top ink from the bottom ink. Furthermore, static SIMS imaging is non-destructive, which is important for the preservation of unique evidence. Prior work demonstrated that ToF-SIMS can correctly determine deposition order of intersections between inks of dissimilar colors[1], and that the order of deposition between fingerprints and ink can be elucidated if the fingerprint is on top of the ink[2]. In order to further test the abilities and robustness of the method, intersections between similar inks need to be examined. In this study, three different black ink samples were tested (Bic^{TM}, Papermate^{TM}, and Staples^{TM} brand pens). Preliminary work produced inconsistent results, and indicated that a more thorough analysis of the primary ions striking the sample and of the polarity of the secondary ions collected needed to be done. Therefore, chemical images of the ink intersections were collected using $Ar\text{-}_{1000}{}^{+}$, $Bi_3{}^{+}$, and $Bi_3{}^{2+}$ primary ions, with both positive and negative secondary ion spectra. Data were analyzed using Principal Component Analysis (PCA) and Multivariate Curve Resolution (MCR). Data analysis included consideration of regions of interest as well as full image analysis, with and without restrictions to the secondary ion mass range. The results point to issues regarding incorrect apparent order of deposition, potentially based on the interactions of inks of different types. This brings the forensic use of ToF-SIMS for determining the order of deposition in ink forgeries into question, and points to the need for further research on factors that can result in incorrect apparent deposition orders.

1. A. He, D. Karpuzov and S. Xu, "Ink identification by time-of-flight secondary ion mass spectrometry", *Surface and Interface Analysis,* **2006**, 38 (4), 854-858.

2. N.J. Bright, R.P. Webb, S. Bleay, S. Hinder, N. Ward, J.F. Watts, K.J. Kirby and M.J. Bailey. "Determination of the Deposition Order of Overlapping Latent Fingerprints and Inks Using Secondary Ion Mass Spectrometry", *Analytical Chemistry*, **2012**, 84, 4083-4087.

9:40am **AS+SS-WeM6 ToF-SIMS Analysis of Aerospace Topcoat Degradation***, **Taraneh Bozorgzad Moghim**, M.L. Abel, J.F. Watts,* University of Surrey, UK

Aircraft coatings are subjected to a multitude of environments during their service life time, including high humidity, extreme temperatures and solar radiation. The major source of degradation derives from ultra-violet (UV) radiation. With commercial aircrafts flying at altitudes between 9 and 13 km, their exposure to UV radiation and ozone significantly increases. Therefore photooxidation of an aircraft topcoat must be understood in order to monitor topcoat degradation. The main laboratory technique used to establish the degradation phenomena from UV radiation is through QUV chambers, however the effect of ozone is not considered in this method. The novelty of the approach used here, is in the use of a desktop cleaner, intended for SEM sample preparation, as the exposure method. This combines the effects of UV and ozone. The topcoat was subject to UV/ozone exposure for varying durations and analysed using time of flight-secondary ion mass spectrometry (ToF-SIMS).

The detail provided by ToF-SIMS is vital in understanding the degradation phenomena and enables a degradation mechanism to be established. ToF-SIMS produces a significant amount of data and therefore when combined with principal component analysis (PCA) a more detailed analysis of the data can be obtained. The main changes observed are the rise of inorganic components with exposure time, as the polymer resin decomposes and the inorganic pigments of the coating are exposed. However this does not describe the degradation of the organic components. Therefore by filtering out the inorganic contributions in the PCA, the changes to the organic components could be isolated and observed. This allows the positive identification of cluster ions of the reactants from the resin and those from the reaction products. In this manner it was possible to deduce the degradation mechanism.

11:00am **AS+SS-WeM10 Surface And Bulk: Are They Always The Same? X-Ray Photoelectron Spectroscopy Study***, **Tatyana Bendikov**, D. Barats-Damatov, B. Butschke, J. Bauer, J. Pellegrino Morono, T. Zell, R. Neumann, D. Milstein,* Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS) is a surface sensitive technique (top 10-15 nm) with sensitivity down to single atomic layer. XPS provides unique information about elemental composition and on the chemical and electronic state of the element in the material. The importance of XPS analysis is essential when the top surface and bulk of the material are different in chemical composition and, consequently, in their properties.

We present here two systems where XPS analysis shows significant differences in elemental composition of the top surface, compared to bulk material characterized by various analytical techniques, such as X-ray crystallography, NMR, EPR, Raman and infrared (IR) spectroscopies, etc.

In the first system, influence of temperature on the crystal packing and secondary structure of phosphovanadomolybdic acid, $H_5PV_2Mo_{10}O_{40}$ was studied.[1] After high temperatures treatment (400-600°C) XPS analysis reveals enrichment of the top surface of the $H_5PV_2Mo_{10}O_{40}$ by amorphous vanadate/phosphate layer.

In the second system, series of iron-PNN complexes were synthesized and characterized in terms of their stability, elemental composition and metal center oxidation state.[2-3] Using example of two complexes, $[(t\mathrm{BuPNN})\mathrm{Fe(NO)_2}]^+[\mathrm{BF_4}]^-$ and $[(t\mathrm{BuPNN})\mathrm{Fe(NO)}\text{-}_2]^{2+}2[\mathrm{BF_4}]^-$, PNN= 2-[(Di-tert-butylphosphinomethyl)-6-diethylaminomethyl)pyridine, it is shown by XPS study that NO ligands are not stable and easily escape from the complex. This reveals changes in structure and in paramagnetic/diamagnetic behavior of these complexes.

1. Barats-Damatov D., Shimon L.J., Feldman I., Bendikov T., Neumann R. *Inorg. Chem.***2015**, *54*, 628-634.

2. Zell T., Milko P., Fillman K.L., Diskin-Posner Y., Bendikov T., Iron M.A., Leitus G., Ben-David Y., Neidig M.L., Milstein D. *Chem. Eur. J.***2014**, *20*, 4403-4413.

3. Butschke B., Fillman K.L., Bendikov T., Shimon L.J., Diskin-Posner Y, Leitus G., Gorelsky S.I., Neidig M.L., Milstein D. *Inorg. Chem.***2015**, *54*, 4909-4926.

11:20am **AS+SS-WeM11 *In Situ* Chemical Imaging of Biointerfaces Using Microfluidics and Molecular Imaging***, **Xiao-Ying Yu,*** Pacific Northwest National Laboratory

The surfaces of aqueous phases and films have unique kinetics and thermodynamics, distinct from the bulk. However, major surface analytical techniques are mostly vacuum-based and direct applications for volatile liquid studies are difficult. We developed a vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI), to enable direct observations of liquid surfaces and liquid-solid interactions using time-of-flight secondary ion mass spectrometry (ToF-SIMS). SALVI was recently applied to investigate biomolecules and biological interfaces in living biofilms and single mammalian cells. Specifically, a variety of hydrated protein thin films were studied, providing the first *in situ* observation of interfacial water or biological water. In the single cell study, ion transport through the ion channel in the cell membrane was mapped in wet cells. In our most recent biofilm research, characteristic fragments of the extracellular polymeric substance (EPS) were obtained for the first time, including proteins, polysaccharides, lipids, polymers, and distinct biomarkers. These species are useful to track the metabolic and electron transfer processes in the microbial communities. For example, biomarkers characteristic of quorum sensing as a result of biofilm response to environmental stressors such as $Cr_2O_7^{2-}$ exposure and subsequent dispersion of the biofilm can be observed using this novel approach. Correlative imaging was employed to achieve a more holistic view of complexed biological systems across different space scales. In addition, electron transfer mechanisms of living biofilms as the electrode material are being studied using the electrochemical version of our microfluidic reactor. Our results demonstrate that interfacial chemistry involving important biomolecules and biological systems can be studied from the bottom up all based on microfluidics. Our transferrable microfluidic reactor sets the analytical foundation toward chemical imaging of complex phenomena occurring in multiple time and length scales, or the mesoscale, underpinning chemical changes at the molecular level in the condensed phase.

11:40am **AS+SS-WeM12 Capturing the Transient Species at the Electrode-Electrolyte Interface by SALVI and Liquid ToF-SIMS***, **Jiachao Yu**, Y. Zhou, X. Hua,* Pacific Northwest National Laboratory*; S. Liu,* Southeast University, China*; Z. Zhu, X.-Y. Yu,* Pacific Northwest National Laboratory

In situ time-resolved identification of interfacial transient reaction species were captured using imaging mass spectrometry, leading to the discovery of unexpected and more complex elementary electrode reactions and providing unprecedented understanding of the reaction mechanism on the electrode surface and solid-electrolyte interface using dynamic molecular imaging. This unique approach was enabled by a vacuum compatible electrochemical microfluidic reactor, namely System for Analysis at the Liquid Vacuum Interface (SALVI). The chemical mechanism of iodine oxidation at the electrode surface was revisited using simultaneous cyclic voltammetry (CV) and dynamic ToF-SIMS. Our dynamic ionic and molecular imaging results suggested that more complex surface reactions exist concerning the gold adlayer formation on the electrode surface, providing the discovery of more short-lived transient species and new insights of elementary electrode reactions unknown in the textbook. Such findings further illustrated the importance of truly observing electron transfer reactions in real-time with high spatial chemical mapping. This innovated approach is suitable for fundamental kinetic studies in electrochemistry at the solid-liquid (s-l) interface or the solid-electrolyte interface with many potential applications such as energy storage, material conversion, and electrocatalysis. The ability to capture and elucidate complex reaction mechanisms at the dynamic s-l interface opens a new door to control, mitigate, design, and engineer reactive pathways toward predictive material synthesis, efficient energy storage, and favorable catalytic conversion.

12:00pm **AS+SS-WeM13 Energy Storage Materials – Investigating the Surface***, **Jonathan Counsell**, S.J. Coultas, C.J. Blomfield,* Kratos Analytical Limited, UK*; C. Moffitt,* Kratos Analytical Limited

Lithium ion batteries are commonly found in home electronic equipment. In recent times there have been significant efforts to improve the durability, cycle time and lifetime decay of the batteries and in particular the electrode/electrolyte material. Novel materials have been developed to also increase the energy storage density. Lithium phosphorus oxynitride (LiPON) has become the most commonly used solid electrolyte thin-film in energy storage devices. Obviously due to the widespread use of this material there is significant interest in understanding the characteristics and properties with a view towards optimisation.

Here we apply XPS and UPS to explore both the surface and bulk properties of several LixPOyNz surfaces prepared via atomic layer deposition ALD [1]. The distribution of elements below the surface is explored via ion and angular-resolved depth profiling methods. This technique has been used extensively across a broad range of applications however the damage caused by impinging ions on the structure of the analysis material has always been a concern for the analyst. More recently Argon gas cluster ion sources have been employed to reduce the chemical damage of organic materials and broaden the range of materials amenable to this type of analysis. Here we extend the application of cluster ions beyond organics to inorganic oxides. Herein we discuss how, with the use of Ar250-3000+ ions, where the energy per atom can be 2.5-40 eV, it is possible to obtain more accurate information regarding the true nature of the LiPON thin-film. A comparison is made with conventional monatomic depth profiles in particular the differences in stoichiometry obtained with the two ion sources. Ion implantation is also discussed as are the unfortunate chemical effects of carbon deposition from organic cluster ions. We will demonstrate how the analyst can now confidently depth profile through inorganic metal oxide thin-films without the worry of reduction or preferential sputtering.

[1] Alexander C. Kozen, Alexander J. Pearse, Chuan-Fu Lin, Malachi Noked, Gary W. Rubloff, DOI: 10.1021/acs.chemmater.5b01654

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 103A - Session HC+SS-WeM

Bridging Gaps in Heterogeneously-catalyzed Reactions

Moderator: Ashleigh Baber, James Madison University

8:00am **HC+SS-WeM1 Vinyl Acetate Formation Pathways and Selectivity on Model Metal Catalyst Surfaces***, **Theodore Thuening**,* University of Wisconsin-Milwaukee

Surface reaction pathways are explored on model single crystal catalyst surfaces using a combination of surface science experiments in ultrahigh vacuum, in-situ monitoring of the surface intermediates during reaction, and by using density functional theory (DFT) calculations. This approach enables detailed reaction pathways to be obtained and is illustrated using palladium catalyzed synthesis of vinyl acetate monomer (VAM). It is shown that vinyl acetate is formed on a Pd(111) and Pd(100) model catalysts via the so-called Samanos pathway, where reaction is initiated by coupling between ethylene and surface acetate species to form an acetoxyethyl intermediate that decomposes by β-hydride elimination to form VAM. The way in which adsorbate coverage affects both reactivity and selectivity is discussed.

8:20am **HC+SS-WeM2 In situ Monitoring of Acetylene Hydrogenation over a Pd/Cu(111) Single Atom Alloy Surface with Polarization Dependent Infrared Spectroscopy***, **Christopher M. Kruppe**, J.D. Krooswyk, M. Trenary,* University of Illinois at Chicago

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 elucidated with Auger spectroscopy (AES), temperature programmed desorption (TPD) of H_2, and PD-RAIRS of CO. After exposing clean Cu(111) and Cu(111) with various Pd coverages to 10 L 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 the areas of the CO peaks in the PD-RAIR spectra is approximately equal to the Pd coverage calculated from peak-to-peak ratios in the Auger spectra. Surface species and gas phase products of C_2H_2 hydrogenation are monitored between 180 K 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 results demonstrate the utility of PD-RAIRS for monitoring the selective hydrogenation of acetylene to ethylene.

8:40am **HC+SS-WeM3 Novel in Situ Techniques for Studies of Model Catalysts***, **Edvin Lundgren**,* Lund University, Sweden **INVITED**

Motivated mainly by catalysis, gas-surface interaction between single crystal surfaces and molecules has been studied for decades. Most of these studies have been performed in well-controlled environments, and has been instrumental for the present day understanding of catalysis. We have in recent years explored the possibilities to perform experiments at conditions closer to those of a technical catalyst, in particular at increased pressures. In this contribution, results from catalytic CO oxidation over Pd single crystal surfaces using High Pressure X-ray Photo emission Spectroscopy (HPXPS), Planar Laser Induced Fluorescence (PLIF), and High Energy Surface X-Ray Diffraction (HESXRD) will be presented.

Armed with structural knowledge from ultra-high vacuum experiments, the presence of adsorbed molecules and gas-phase induced structures can be identified, and related to changes in the reactivity and/or to reaction induced gas-flow limitations. The strength and weaknesses of the experimental techniques will be discussed.

9:20am **HC+SS-WeM5 Metastable Cluster Formation and Polymorphism of Hydrogen-bonding Molecules on Gold are a Consequence of the Pulse-deposition of a Solution into Vacuum***, **Ryan Brown**, S.A. Kandel,* University of Notre Dame

A primary motivation in studying the assembly of molecules at an interface is to determine the underlying principles which drive the spontaneous formation of supramolecular structures under specific environmental conditions, with the ultimate goal being an understanding which allows control over such processes. Recently we have postulated the importance of solution-phase cluster formation during the pulse-deposition, in vacuum, of small organic and organometallic molecules which contain strong hydrogen bonding components, namely carboxylic acid functional groups, in addition to weak hydrogen bonding donors. Specifically, we have studied the cluster formation of 1,1'-ferrocenedicarboxylic acid, $Fc(COOH)_2$, which has been pulse deposited on Au(111)-on-mica substrates. We employed low temperature scanning tunneling microscopy (LT-STM) to observe which molecular clusters persist at the interface following pulse-deposition from solution. We subsequently performed annealing experiments to determine which of these species represent stable conformations, and which are metastable species formed in the solution droplet during deposition. LT-STM images of $Fc(COOH)_2$ show a coexistence between dimer, chiral hexamer, and square tetramer clusters. Since the bulk crystal structures for $Fc(COOH)_2$ are all comprised entirely of molecular dimers, the most stable 2D supramolecular structure likely is some array of dimers, whereas the other species present are metastable. We attribute the initial strong presence of metastable species to the formation of clusters in solution, followed by their precipitation as predicted by Ostwald's rule, then their adsorption on to the substrate in a kinetically-trapped conformation. Electrospray ionization mass spectrometry (ESI-MS) of $Fc(COOH)_2$ solutions supports the presence of hexamer clusters in solvent droplets, which confirms the possibility that the chiral hexamers observed after deposition precipitate from the solution droplet. Sequential mild annealing stepsof this surface results in the formation of linear rows of square tetramers, chiral dimer domains, and eventually tilted dimer arrays. The prevalence of each of these species is related to the surface's thermal history, and this is characteristic of a system evolving under kinetic control. We propose that injection of solution into a vacuum environment can be exploited to produce supramolecular 2D-structures not observed in the bulk crystal, and that the frequency of nature of the metastable species present should be dependent on variables such as the solution concentration, solvent, and droplet size.

9:40am **HC+SS-WeM6 Understanding the Activity of Pt-Re Bimetallic Clusters on Titania and Pt-Re Alloy Surfaces in the Water Gas Shift Reaction***, **Donna Chen**, A.S. Duke, K. Xie, A.J. Brandt, T.D. Maddumapatabandi,* University of South Carolina

The chemical activities of bimetallic Pt-Re clusters supported on TiO_2(110) and single-crystal Pt-Re alloy surfaces are investigated as model systems for understanding Pt-Re catalysts in the water gas shift (WGS) reaction. The activities of these Pt-Re bimetallic surfaces are studied 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. Bimetallic clusters consisting of a Re core covered by a Pt shell have turnover frequencies that are almost twice as high as that of the pure Pt clusters at 160 °C. Furthermore, the Re in the active bimetallic clusters remains in its metallic state because Re is not readily oxidized when it remains subsurface; there is no evidence that ReO_x is active in promoting the WGS reaction. Pure Re clusters are not active for the WGS reaction, and bimetallic clusters with significant Re at the surface are less active than pure Pt clusters. Surface Re is oxidized under reaction conditions and sublimes as Re_2O_7. Post-reaction infrared spectroscopy studies show that CO and hydroxyls are detected on the surface.

11:00am **HC+SS-WeM10 Fundamental Studies of the Water-gas Shift and CO_2 Hydrogenation on Metal/oxide Catalysts: From Model Systems to Powders***, **Jose Rodriguez,*** Brookhaven National Laboratory **INVITED**

In this talk, it will be shown how a series of *in-situ* techniques {X-ray diffraction (XRD), pair-distribution-function analysis (PDF), X-ray absorption spectroscopy (XAS), environmental scanning tunneling microscopy (ESTM), infrared spectroscopy (IR), ambient-pressure X-ray photoelectron spectroscopy (AP-XPS)} can be combined to perform detailed studies of the structural, electronic and chemical properties of metal/oxide catalysts used for the production of hydrogen through the water-gas shift reaction (WGS, $CO + H_2O \rightarrow H_2 + CO_2$) and the hydrogenation of CO_2 to methanol (MS, $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$). Under reaction conditions most WGS and MS catalysts undergo chemical transformations that drastically modify their composition with respect to that obtained during the synthesis process. The active phase of catalysts which combine Cu, Au or Pt with oxides such as ZnO, CeO_2, TiO_2, CeO_x/TiO_2 and Fe_2O_3 essentially involves nanoparticles of the reduced noble metals. The oxide support undergoes partial reduction and is not a simple spectator, facilitating the dissociation of water, or the adsorption of CO_2, and in some cases modifying the chemical properties of the supported metal. Therefore, to optimize the performance of these catalysts one must take into consideration the properties of the metal-oxide interface. IR and AP-XPS have been used to study the reaction mechanism for the WGS and MS on the metal/oxide catalysts. Data of IR spectroscopy indicate that formate species are not necessarily involved in the main reaction path for these reactions on Cu-, Au- and Pt-based catalysts. Thus, a pure redox mechanism or associative mechanisms that involve either carbonate-like (CO_3, HCO_3) or carboxyl (HOCO) species should be considered. In the last two decades, there have been tremendous advances in our ability to study catalytic materials under reaction conditions and we are moving towards the major goal of fully understanding how the active sites for the production of hydrogen through the WGS or the hydrogenation of CO_2 to methanol actually work.

11:40am **HC+SS-WeM12 The Use of EC-STM to Study the Chemical Reactivity and Nanoscale Structure of Metal Surfaces***, A. Phillips, L. Jackson, H. Morgan, G. Jones, **Erin Iski,*** University of Tulsa

In the development of surfaces as efficient catalysts, it is critical to understand and control the surface reactivity in a defined manner. Electrochemical Scanning Tunneling Microscopy (EC-STM) is an advantageous 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 harness the chemical reactivity of the surface. This technique offers a unique window to study catalysis at conditions outside of a UHV environment, specifically at ambient temperatures and in liquids. Also, cyclic voltammograms (CVs) can be generated to provide specific information regarding the nature of the redox events occurring at the surface. Within this framework, it is possible to study how certain surfaces can become activated and/or deactivated as a result of electrochemical manipulation. One specific example of a thermally deactivated surface is a single Ag layer on a Au(111) crystal. The Ag layer is deposited on the Au(111) surface using Underpotential Deposition (UPD), which is an extremely controllable electrochemical technique for the application of a monolayer (or less) of a metal onto a more noble metal. Surprisingly, this atomically-thin Ag layer when formed in the presence of halides remains on the Au surface after heat treatments as high as 1,000 K. Importantly, thermal stabilization can be contrasted and compared with catalytic activity in which chlorine has shown to be a promoter of ethylene epoxidation over Ag(111), demonstrating why this system is intriguing from multiple vantage points. From a general standpoint, EC-STM offers an environmentally unique handle on how the chemical reactivity of a metal surface can be altered and how that surface can then be studied on a fundamental level.

12:00pm **HC+SS-WeM13 Formation and Stability of Surface Oxides on Ag(111)***, **Daniel Killelea**, J. Derouin, R.G. Farber, M.E. Turano,* Loyola University Chicago*; E.V. Iski,* The University of Tulsa

A long-standing challenge in the study of heterogeneously catalyzed reactions on silver surfaces has been the determination of what surface phases are of greatest chemical importance. This is due to the coexistence of several different surface phases on oxidized silver surfaces. A further complication is subsurface oxygen (O_{sub}). O_{sub} are O atoms dissolved into the near surface of a metal, and are expected to alter the surface in terms of chemistry and structure, but these effects have yet to be well characterized. We studied oxidized Ag(111) surfaces after exposure to gas-phase O atoms with a combination of surface science techniques to determine the resultant surface structure; we observed that once 0.1 ML of O_{sub} has formed, the surface dramatically, and uniformly, reconstructs to a striped phase at the expense of all other surface phases. Furthermore, O_{sub} formation is hindered at temperatures above 500 K. We also observed a coexistence of several surface oxides at intermediate deposition temperatures, and the predominance of the *p*(4x5√3) surface reconstruction at elevated temperatures.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+SS+TF-WeM

Probing Electronic Properties

Moderator: Carl Ventrice, Jr., SUNY Polytechnic Institute

8:00am **SP+SS+TF-WeM1 Local Probe Investigation of 1D Structures and Interfaces in 2D Materials***, **Chenggang Tao,*** Virginia Tech **INVITED**

Emerging two-dimensional (2D) materials, such as graphene and atomically thin transition metal dichalcogenides, have been the subject of intense research efforts for their fascinating properties and potential applications in future electronic and optical devices. The interfaces in these 2D materials, including domain boundaries and edges, strongly govern the electronic and magnetic behavior and can potentially host new quantum states. On the other hand, these interfaces are more susceptible to thermal fluctuation and external stimuli that drive mass displacement and generate disorder. In this talk we will present our scanning tunneling microscopy (STM) and spectroscopy (STS) explorations of edges of few layered molybdenum disulfide (MoS_2) nanostructures with unique structural and electronic properties and show how step edges on titanium diselenide ($TiSe_2$) surfaces change dynamically due to electrical fields. We will also discuss temperature evolution of quasi-1D C_{60} nanostructures on graphene. Through careful control of the subtle balance between the C_{60} surface mobility and the linear periodic potential of rippled graphene, C_{60} molecules can be arranged into a novel 1D C_{60} chain structure, and this chain structure can further transition to a compact hexagonal close packed stripe structure by tuning the annealing temperature.

8:40am **SP+SS+TF-WeM3 Investigation of Electronic Structures from Monolayers to Multilayers in Charge Transfer Complex, TTF-TCNQ using Low-temperature Scanning Tunneling Microscopy/Spectroscopy***, **Seokmin Jeon**, P. Maksymovych,* Oak Ridge National Laboratory

The properties of few-layer molecular films are in general distinct from both bulk and monolayer phases, particularly in the case of metallic substrates, whose high-density electronic structure dominate the monolayer electronic structure and hamper characterization of the intrinsic properties of the molecular layer. This is especially true for charge transfer molecular solids, whose interesting electronic properties derive from a subtle alignment of each individual component's states, balance of dielectric screening, long-range electrostatic interactions, and relative molecular geometry. In contrast to vast effort on bulk phase study of the historic organic charge-transfer complex, TTF-TCNQ, study of its low-dimensional phases has been limited to monolayer phases. We investigated the evolution of the electronic structure of TCNQ and TTF-TCNQ multilayers using STM/STS at 4.3 K.

Thanks to submolecular resolution STM data and DFT calculations we were able to accurately determine the stacking relationship between the overlying layer and the underlying layer at an atomic scale. In such a well-defined layered model structure, we scrutinize the electronic structures of multilayered TCNQ and TTF-TCNQ using STS. Double-periodic charge ordering and Coulomb gap features are observed in the bilayer TTF-TCNQ. The effect of substrate variation (Ag, Au, and HOPG) on multilayer growth and electronic properties are discussed. The STS data from the multiple combinations of adsorbates and substrates allow us to assign states reliably and understand of transition of the surface, molecular, and charge transfer states clearly in the multilayer systems.

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

9:00am **SP+SS+TF-WeM4 Investigation of Initial Stages of Oxidation of Ni-Cr and Ni-Cr-Mo Alloys by Scanning Tunneling Microscropy/Spectroscopy (STM/STS)***, **Gopalakrishnan Ramalingam**, P. Reinke,* University of Virginia

Ni-Cr based superalloys are excellent candidates for use in highly corrosive environments due to their exceptional oxidation and corrosion resistance. Our work focuses on unraveling the initial reaction steps of alloy oxidation as a function of composition, moving from the clean Ni-surface to a Ni-base alloy with 33wt% Cr. In the study presented here, we used STM/STS to investigate the initial stages of oxidation reaction in Ni-Cr (0-35wt.% Cr) alloys and the impact of Mo (2-10 wt.%) on the reaction. We developed spectroscopy maps which yield highly coveted information on the spatial distribution of oxide nuclei and the transition from chemisorbed oxygen to oxide. The STS maps capture the evolution of oxide during various stages of oxidation and provides valuable insight into the reaction as a function of composition of alloy.

Cr is the main alloying addition in Ni-based superalloys and the minimum amount of Cr necessary to form a continuous, passive oxide layer is 6-13 wt.% based on empirical observations. The passivating quality of an oxide layer strongly depends on the initial nucleation of the oxide, the oxide growth during continued oxidation, and eventual coalescence to form a complete oxide layer. However, the effect of Cr content on the initial nucleation and growth behavior of the oxide is not well understood. Similarly, the underlying mechanisms at the atomic scale and the role of electronic structure changes due to Mo addition are not well understood.

In this study, alloy thin films grown on MgO(100) substrates in an ultrahigh vacuum chamber are oxidized in situ at 300 °C with O_2 exposure up to 130 L. In the initial stages of oxidation (0.5-7 L of O_2), oxide nuclei are initially formed at the step-edges with some nucleation also present on the flat terraces. Subsequent oxygen exposure (>30 L) results in growth of existing oxide islands with additional nucleation of oxide. The amount of oxygen required for complete oxide coverage depends strongly on the Cr content of the alloy: >85% of the surface is covered with oxide in a Ni-14wt.%Cr alloy after 80 L oxidation while the same coverage is achieved in Ni-33wt.%Cr alloy after only 11.5 L. In contrast, we do not observe a complete oxide layer on Ni surface even after 180 L oxidation. Scanning tunneling spectroscopy maps provide spatially resolved electronic structure information and the variation of bandgap of the oxide as a function of oxide thickness and Cr content will be discussed. Preliminary data on the changes in the atomic and electronic structure of the thin film and oxidation behavior due to the addition of Mo will be presented.

9:20am **SP+SS+TF-WeM5 Au(111) Characterization, Single Atom Manipulation and Si(100):H Surface Imaging by LT-UHV-4 STM***, **Corentin Durand**, D. Sordes, C. Joachim,* CNRS, France **INVITED**

Advance in nanotechnology requires the development of new instruments capable of imaging, communicating, manipulating and measuring at the atomic scale. The performances of the new ScientaOmicron LT-UHV 4-STM microscope have been certified by a series of state-of-art STM experiments on an Au(111) surface at 4.2 K [1]. During the STM operation of the 4 STM scanners (independently or in parallel), a Z stability of about 2 pm per STM was demonstrated. With this LT-UHV 4-STM stability, single Au atom manipulation experiments were performed on Au(111) by recording the pulling, sliding and pushing manipulation signals. Jump to contact experiments lead to perfectly linear low voltage I-V characteristics on a contacted single Au ad-atom with no need of averaging successive I-V's. Our results show that the 4 scanners of this new instrument working in parallel have performances equivalent to single tip state-of-art LT-UHV-STM. Two tips surface conductance measurements were performed on Au(111) using a lock-in technique in a floating sample mode of operation to capture the Au(111) surface states via two STM tips dI/dV characteristics. The capabilities of this microscope being demonstrated, we now move on to our next project, the realization of atomic devices. The hydrogen passivated Si(100) surface is a good candidate to achieve this goal. Here, I will show our preliminary results regarding the investigation of this surface and its topography. The surface has been prepared by a "wafer-bonding" method [2]. Large scale STM images show that this technique provides large and clean terraces essential to the fabrication of atomic circuits. Atomic resolution imaging enables us to confirm the position of the dimers, these latter ones having a different aspect depending on the polarity of the tunneling junction [3]. Finally, I will introduce the route of our project, the different steps we must achieve in order to build up a device made of few atoms on this surface [2].

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

[2] M. Kolmer et al. Appl. Surf. Sci., vol. 288, p. 83, 2014

[3] T. L. Yap et al. Surf. Sci., vol. 632, p. L13, 2015

11:00am **SP+SS+TF-WeM10 Heterochiral to Homochiral Transition in Pentahelicene 2D Crystallization induced by 2nd-layer Nucleation***, **Anaïs Mairena**,* Universität Zürich, Switzerland

Chirality is ubiquitous in our world (human body, pharmaceutics, liquid crystals…). Nevertheless, the principles of intermolecular recognition are still poorly understood. Therefore, it is not possible to predict the outcome of crystallization, which is still the most important method to separate chiral molecules into their enantiomers, or to explain why a minority of chiral compounds crystallize into conglomerate. A promising approach towards a better understanding of chiral interactions is the study of self-assembly of chiral molecules on single crystal surfaces with STM (sub-molecular resolution).

We studied the 2D self-assembly of racemic-pentahelicene ([5]H, $C_{22}H_{14}$) on Cu(111) with STM. Adsorption of [5]H leads, already at very low coverages to formation of homochiral pairs, i.e. both molecules have the same handedness.

At coverages close to the saturated monolayer, two distinct long-range ordered structures have been observed. Both structures have the homochiral pairs as building blocks. However, while one structure consists of a conglomerate of homochiral domains, the second structure is racemic, i.e. composed of homochiral pairs with opposite handedness. At monolayer coverage, only the racemic structure prevails. Above monolayer coverage, the dense racemate phase in the monolayer disappears on the expense of a homochiral conglomerate phase with lower density due to 2nd-layer-nucleation. Our results indicate that a long-range chiral communication between 2nd layer islands and other areas on the surface are at work.

These findings are also compared with those obtained for heptahelicene ($C_{30}H_{18}$) on Cu(111). A surface-mediated selection mechanism, taking different intermolecular interactions into account, will be presented.

11:20am **SP+SS+TF-WeM11 Two-stage Chiral Selectivity in the Molecular Self-Assembly of Tryptophan***, **Nathan Guisinger**,* Argonne National Laboratory*; B. Kiraly,* Northwestern University*; R. Rankin,* Villanova University

Both chirality and molecular assembly are essential and key components to life. In this study we explore the molecular assembly of the amino acid tryptophan (both L- and D- chiralities) on Cu(111). Our investigation utilizes low temperature scanning tunneling microscopy to observe resulting assemblies at the molecular scale. We find that depositing a racemic mixture of both L- and D- tryptophan results in the assembly of basic 6 molecule "Lego" structures that are enantiopure. These enantiopure "Legos" further assemble into 1-dimensional chains one block at a time. These resulting chains are also enantiopure with chiral selectivity occurring at two stages of assembly. Utilizing scanning tunneling spectroscopy we are able to probe the electronic structure of the chiral Legos that give insight into the root of the observed selectivity.

11:40am **SP+SS+TF-WeM12 Mask Free Approach to Selective Growth of Transition Metal Dichalcogenides Heterostructures enabled with Scanning Probe based Nanolithography***, R. Dong, L. Moore, N. Aripova, C. Williamson, R. Schurz,* Saint Louis University*; L.E. Ocola,* Argonne National Laboratory*; **Irma Kuljanishvili**,* Saint Louis University

Advances in graphene research ignited interest in other type of two-dimensional (2D) atomic crystals, such as hexagonal boron nitride and layered transition metal dichalcogenides (TMDCs). Among these new types of 2D materials, the applications of TMDCs in logic electronics and optoelectronics are promising because of their sizable bandgaps and natural stability. The techniques which enable heterostructure formation with different TMDCs systems have provided further solution to the design of high performance electronic devices such as those for photovoltaics and optoelectronics. The existing heterostructures fabrication methods, based on mechanical exfoliation and/or wet chemical transferring rely on traditional fabrication methods such as photo-and e-beam lithography.

To realize the selective growth and layered assembly of heterostructures at predefined location, here, we report on application of mask free, scanning probe based direct writing method. With the use of AFM cantilevers and developed water based "inks", we demonstrate arrays of MoS_2 and WS_2 dots and ribbon arrays at predefined locations on variety of substrates.

Employing this SPM based patterning method we have also fabricated MoS_2/WS_2 heterostructures of sub-micrometer scales in a controlled fashion. The quality of MoS_2/WS_2 heterostructures was confirmed by Raman spectroscopy, AFM characterization and electrical transport measurements. Our mask free nanolithography approach offers an alternative route for patterning and growth of TMDCs with added benefit of potential reduced contamination of the TMDCs surfaces and interfaces between materials and substrates. It demonstrates a promising unconventional technology for fabrication of high quality TMDCs heterostructures in convenient manner capable of nanoscale precision.

Acknowledgements

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. I.K. acknowledges support of NSF MRI program (Award No. 1338021), and the Saint Louis University seed funds.

12:00pm **SP+SS+TF-WeM13 Non-Destructive Electrical Depth Profiling across Nanometric SiO_2 Layers***, **Hagai Cohen**,* Weizmann Institute of Science, Israel*; A. Givon,* Tel Aviv University, Israel

The access to sub-nm scale depth information in thin dielectric layers, considering both the compositional and the electrical sub-surface characteristics, is challenging. A remarkable answer may be provided by CREM (chemically resolved electrical measurements), a technique based on x-ray photoelectron spectroscopy (XPS). CREM exploits the chemical contrast within a given structure to gain rich electrical information, or alternatively, apply electrical tests to gain improved structural&compositional analyses. Yet, for compositionally uniform domains, CREM becomes rather insensitive to the fine profiling details. Here, we show that this principal limitation can be overcome and the CREM resolution be improved significantly. Applied to nanometric silica layers, we reveal hidden impurity concentration profiles and further correlate them with the depth-dependent dielectric quality. Based on this leap improvement in resolution and sensitivity, our advanced CREM analysis promises diverse applications in device contact-free electrical studies.

Surface Science
Room 104D - Session SS+2D-WeM

Synthesis, Characterization, and Surface Science of Novel Materials and Interfaces

Moderator: Talat Rahman, University of Central Florida

8:00am **SS+2D-WeM1 Early Stages of the Thermal-Induced Mobility of Ag in SiC***, **Daniel Velázquez**, R. Seibert, J. Terry,* Illinois Institute of Technology

Tri-structural isotropic (TRISO) particles are the fuel of choice for very-high temperature reactor technology. At the core, these spherical particles consist of an inner fuel kernel of UO2, UC2 or a combination of both, which is coated radially outward by successive layers of low density pyrolytic graphite, an inner high density pyrolytic graphite layer, silicon carbide (SiC) and an outer high density pyrolytic graphite layer. SiC is the main diffusion barrier against the release of fission products due to its hardness and high melting point. Nonetheless, irradiation testing of TRISO particles indicates that trace amounts of metallic fission products, such as Ag (which as a ~41 day half-life), diffuse through SiC. Competing theoretical and experimental observations that indicate that Ag diffuses through the bulk and through grain boundaries. Diffusion through grain boundaries is usually amplified due to the formation of large grains upon crystallization by heating. This leads to the formation of triangular micro pits in thin films, suggesting that a 3D version of this form of crystallization could facilitate even more the release of Ag. Previously XAFS and XPS have shown that Ag remains metallic in a SiC matrix, indicating that bulk diffusion is perhaps interstitial rather than substitutional. In this work we discuss the mobility of Ag films enclosedon layers of 3C-SiC by analyzing SEM images taken before and after annealing. Image analysis supported by surface spectroscopic and crystallographic techniques are used in order to estimate the release of Ag through SiC for Ag interlayers at various thicknesses and annealing temperatures. Preliminary analysis by SEM/EDS show that upon annealing Ag escapes through the SiC surface by three different mechanisms, which roughly in chronological are: 1) escape through triangular pits and grain boundaries in SiC; 2) agglomeration and formation ofsub-surface blisters which eventually rupture; 3) diffusion through the bulk of SiC when the trapped amounts of Ag are insufficient to form large blisters. During the third mechanism, we still observed sub-surface mobility in the form of dendritic paths. When the starting amount of Ag is reduced sub-surface diffusion is limited and the release of Ag is dominated by the escape through the triangular pits of SiC and bulk diffusion.

8:20am **SS+2D-WeM2 Quantitative Chemical State base on XPS Energy Scan Image Applied to Ni Fe corroded Samples***, **Vincent Fernandez**, J. Keraudy,* Université de Nantes, France*; N. Fairley,* Casa Software Ltd, UK*; P.Y. Jouan,* Université de Nantes, France

1. Introduction

Corrosion is a natural phenomenon where metals have a tendency to revert back to their natural, lower energy state. During many years, the most effective corrosion protection systems were based on the use of chromate-rich surface treatments. However, recently, the legislation imposed by the european commission, REACH (Registration, Evaluation, Authorization and Restrictions of Chemicals) prohibited the use of hexavalent chromium. Many alternatives have been explored so far, including the protection with monolayer and/or multilayers of thin films (Cr, CrN, Ti, TiN, NbN) deposited by magnetron sputtering process. Corrosion is a physical-chemical interaction between the metal and its environment. Most hard coatings (TiN, CrN, NbN) possess an higher corrosion resistance than less noble materials like steel, Al or Mg alloys. When the coatings are deposited on such less noble substrates and exposed to a corrosive atmosphere (ex : NaCl), the coated parts suffer from serious corrosive attack (pitting corrosion) due to inherent coating defects or inhomogeneities . This kind of corrosion is localized to the defect area and is characterized by the anodic dissolution of the substrate material with a high anodic current density at the defect site. It is generally called galvanic corrosion. In this study, Nickel thin film (2 micrometers) was deposited on steel substrate (XC38) using Direct Current Magnetron Sputtering from a Ni target. In order to simulate the corrosive attack, the coated part was exposed to a corrosive medium, i.e salt spray test. The test was conducted under continuous spray (24 hours) conditions (5wt.% NaCl) at a temperature of 35 °C according to the ASTM B117 standard procedure.

The morphology and the chemical environment of the corrosion products were analyzed respectively by optical microscopy and XPS investigations.

2. Results

The samples have conducting and isolating regions to avoid spatial differential potential the samples were measured in a floating condition. The Parallel XPS images of 128 pixels by 128 pixels where done with FOV of 900 x 900 microns at an energy resolution of about 1eV and an energy step of 0.2 eV for O 1s, Na KLL, Ca 2p, C 1s, Ni 3p and Fe 3p with charge compensation. Ni and Fe were measure in one region. To treat the 735 images corresponding of more than 1.2 10^7 intensity points, images were smoothed and projected on PCA images. All images were projected on 6 abstract factors. Then images were converting in 81920 spectra. After spectra quantification, energies regions were converting back in quantitative images. Then Fe map was classified in 5 false colors part by intensity.

8:40am **SS+2D-WeM3 Novel Approaches to Form Organic-Inorganic Interfaces: Parallels between Coupling and Surface Modification Schemes in Vacuum and in Wet Chemistry***, **Andrew Teplyakov**,* University of Delaware

Recent interest towards controlled formation of organic-inorganic interfaces affected greatly the approaches used for surface modification of semiconductors. Despite substantial progress in designing chemical pathways for surface modification of these materials and synthetic capabilities to build a variety of precursor molecules, two major issues remain: 1) Can the same level of precision achieved for surface characterization in vacuum be achieved for surfaces modified by wet chemistry methods; and 2) Can the elemental and compound semiconductor surfaces be modified with chemical groups that are both oxygen- and carbon-free. These two questions will be addressed by drawing parallels between cyclocondensation processes on modified semiconductor surfaces and cycloaddition in vacuum. Mixed surface modification schemes will be discussed for silicon and ZnO materials to produce high-coverage chemical “hooks” and the use of these functionalities will be demonstrated for initial stages of film deposition or depositing large constructs (nanoparticles and buckyballs) by chemical addition to produce strong covalent bonds. The addition across double bonds of carbonaceous constructs and the production of chemical bonds by straightforward chemical reactions will be discussed. The reactions for producing amino-functionalities and the platforms for “click” reactions will be presented. The experimental evidence of the reactions will be based on infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and a combination of microscopic techniques. The selected results of the experimental work will be compared with the experimental observables predicted by density functional theory (DFT).

9:00am **SS+2D-WeM4 Adsorption of Hetero-bifunctional Urea on Ge(100)-2x1 Surface***, **Tania Sandoval**, S.F. Bent, A.M. Crow,* Stanford University

Organic functionalization of Group IV semiconductor surfaces is of interest due to the need for new pathways in surface chemistry modification. This is important in applications such as molecular layer deposition, molecular electronics, and biosensors where the ability to control and tune surface properties requires a deep understanding of the interactions between molecules and solid surfaces. In this study, adsorption of the heterobifunctional urea molecule on the Ge(100)-2x1 surface was investigated. Both the amine and carbonyl group of the urea molecule are known to react with the Ge surface. The aim of this study is to determine if any preferential reaction pathways exist and to understand the driving forces toward the final products.

Density functional theory (DFT) calculations suggest that NH_2 dissociation is the most thermodynamically favorable pathway for the single reaction. The reaction can occur through two possible precursor states: a nitrogen dative bond with the surface or an oxygen dative bond that can further undergo an enolization reaction. Interestingly, the oxygen dative bond is 7 kcal/mol more stable than the nitrogen bond, suggesting a preference for the latter reaction pathway. Furthermore, calculations show that the dual reactions provide less stabilization gain and a higher kinetic cost than single reactions, as the dual NH_2 dissociation has an activation barrier greater than 30 kcal/mol and only provides 5 kcal/mol of additional exothermicity, indicating that the urea molecule will likely react only through a single functional group. X-ray photoelectron spectroscopy (XPS) and multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy were used to determine the final reaction products. Results suggest that urea adsorbs on Ge(100) forming a mix of surface products. One of the products can be identified by the downshift in binding energy of the N(1s) XP peak and the Ge-H stretching mode in IR as NH_2-dissociated urea on Ge. This assignment is also consistent with the presence of a carbonyl group in the IR and XPS spectra, which is expected to remain unchanged in this surface configuration. Another reaction product exists that is evident by second O(1s) and C(1s) XPS peaks downshifted from that of the parent urea molecule, suggesting a loss of the carbonyl group by a reaction with a more electropositive atom. Moreover, coverage results support our DFT findings by suggesting that each urea molecule will occupy a Ge dimer by reacting through a single functional group per molecule.

9:20am **SS+2D-WeM5 Electronic Structure of Ferroelectric Nanodomains***, **Erie Morales**, C. Perez, M. Brukman, D. Bonnell,* The University of Pennsylvania

The local measurement of structure and properties enabled by scanning tunneling microscopy and atomic force microscopy in conjunction with systematic control of in situ environments has yielded insight into the fundamental behavior of ferroelectric compounds. Many atomic structures on BaTiO3 surfaces have been determined, the thermodynamic stability of structures on (001) surfaces has been described, and the polarization dependence of several classes of surfaces reactions has been demonstrated. In addition the polarization behavior at the nanoscale has received much attention.

Here we report unusual impact of local poling on the electronic structure of ferroelectric surfaces. Scanning Tunneling Microscopy in situ poling was performed on BaTiO3 (001) in ultra high vacuum (UHV). The voltage pulse produces apparent anti-parallel ferroelectric domains. Domain size can be controlled by changing conductivity of the crystal and/or by changing the bias set point; the smallest domain we pole is 24 nm. We use a 4-D analysis of geometric and electronic structure data to characterize the variations in electronic structure. Patterns of variations in the surface band gap are consistent with existing theoretical calculations of anti parallel domain orientations.

9:40am **SS+2D-WeM6 Using Data Analytics and Informatics in Understanding Enhanced Conductivity, Mobility, and Transparency in ITO Bearing ZrO_2 and reduced SnO_2***, **Timothy Peshek**,* Case Western Reserve University*; J.M. Burst, T. Coutts, T.A. Gessert,* National Renewable Energy Laboratory

We deposited high quality tin-oxide-doped indium oxide (ITO) by RF magnetron sputtering with varying oxygen partial pressure in the sputter ambient and using targets with a nominal concentration of 5 wt% SnO_2, instead of a typical 10 wt%, and between 0-3 wt% ZrO_2. We demonstrate mobilities of $>$45 cm^2/Vs for sputtered ITO films at zero added oxygen. We demonstrate resistivities in the range of 10^{-5} Ω-cm at zero added oxygen with 1 wt% ZrO_2 added, mobilities at >55 cm^2/Vs and the films showed a modest increase in optical transmission with increasing Zr-content.orptio

Hypothetically the increase in mobility that apparently accompanies the addition of ZrO_2 yields enhanced optical clarity in the IR due to reduced free carrier absorption from reduced doping concentration for any given resistivity.

Anomalous behavior was discovered for films with no Zr-added, where a bimodality of high and low mobilities were discovered for nominally similar growth conditions. We examined this anomalous behavior using modern data science and visualization techniques of big data and materials informatics. We used these techniques to gain insights into the mechanistic behavior of the relationship between stoichiometry, process variables, material morphology and electrical properties. We will summarize these findings and describe the methods used in the analysis and a path forward for continuing utilizing data analytics in material characterization and learning.

11:00am **SS+2D-WeM10 Surface Composition and Atomic Structure of Topological Insulator Materials***, **Jory Yarmoff**, W. Zhou, H. Zhu,* University of California - Riverside **INVITED**

A topological insulator (TI) is a two-dimensional material that behaves as an insulator in the bulk, but conducts along the surface via topologically protected surface states. TI's have attracted intense interest because of their fundamental importance combined with great potential for applications in areas such as spintronics and quantum computation. Because the critical electronic states in TI's are localized in the near-surface region, it is critical to understand their surface composition, surface atomic structure and surface chemistry, and there are several outstanding issues that have not been fully resolved. For example, the materials are often naturally doped leading to the Fermi energy residing in the conduction band. Some materials have also been observed to change over time, the so-called "aging effect". In addition, the surface termination of the prototypical TI, Bismuth Selenide (Bi_2Se_3), has been an area of recent debate. Although some studies have demonstrated that the cleaved surface is terminated with Se, as expected from the bulk crystal structure, there are other reports that show either a Bi-rich or mixed-termination.

We are using low energy ion scattering (LEIS), in conjunction with other surface analysis tools, to investigate the surface composition and atomic structure of TI materials prepared in numerous ways. LEIS is uniquely suited to measure surface termination and atomic structure, as it provides the elemental identification of the near-surface region and can be deployed to probe only the outermost atomic layer. We compared surfaces prepared by *ex situ* cleaving, *in situ* cleaving and Ar^+ ion bombardment and annealing (IBA) in ultra-high vacuum. LEIS measurements do not indicate any substantial differences between the Se-terminated surfaces prepared by IBA or *in-situ* cleaving. Samples inserted into the vacuum chamber following *ex-situ* cleaving are less well-ordered, show adsorbed oxygen and can be either Se-terminated or Bi-rich, which suggests a critical dependence on the level of contamination. We have also used molecular beam epitaxy to investigate the structure and stability of Bi overlayers grown on Bi_2Se_3. Additional experiments involve exposure of clean surfaces to gaseous species such as O_2, H_2 and Br_2.

11:40am **SS+2D-WeM12 Impact Collision Ion Scattering Spectroscopy of Bi_2Se_3 and Bi/Bi_2Se_3***, **Weimin Zhou**, H. Zhu, J.A. Yarmoff,* University of California - Riverside

Bismuth selenide (Bi_2Se_3) and isolated bilayers of bismuth both behave as topological insulators, which are two-dimensional materials that conduct along the surface through topological surface states (TSS). These materials show great promise for use in spintronics and quantum computation. Because the TSS are located at the surface, it is important to understand the relationships between the surface atomic and electronic structures. Low energy ion scattering (LEIS) is a simple, but powerful surface sensitive technique that is ideal for structural analysis. LEIS, using Na^+ projectiles, is employed here in two distinct modes. First, time-of-flight (TOF) spectra are collected using low index incidence directions. This allows for a direct measure of the surface termination with minimal beam damage. Second, impact collision ion scattering spectroscopy (ICISS), which involves the collection of angular distributions using a large scattering angle, is employed to study the structure of the outermost few atomic layers. This work investigates the surfaces of clean Se-terminated Bi_2Se_3 and after a Bi bilayer has been grown on top by molecular beam epitaxy (MBE). Molecular dynamics (MD) simulations of ICISS are compared to the experimental data in order to ascertain the surface structures.

12:00pm **SS+2D-WeM13 Feature Scale Simulation for Materials Processing**, ***Paul Moroz,*** TEL Technology Center, America, LLC; *D.J. Moroz,* University of Pennsylvania

Modern materials processing often includes complex chemistries and surface interactions, and variety of species incoming to the wafer from gas and/or plasma in the chamber. It also often involves many time-steps, each one utilizing different chemistry and different gas/plasma parameters resulting in time-varying composition of fluxes coming to the wafer, and different energy and angular distributions of incoming species. Chemically or physically active species interact with material surfaces, generally resulting in etching, deposition, and implantation, and such processes might even happen together at the same time. The FPS3D feature scale simulator [1-3] is capable of handling very different and complex cases due to its special structure and numerical techniques, from atomic layer etching and atomic layer deposition to large-scale Bosch processing. Numerical models of surface and molecular interactions are flexible enough to describe most general cases. For this presentation, we selected three types of simulation cases. The first type considers simulation of mostly etching and implantation, such as during Si etching by chlorine-argon plasma. The 2nd type considers ALE (atomic layer etch) when etching is done by a cyclic process of surface passivation/activation with the following process of etching/removal of a single atomic layer per cycle or per a few cycles, allowing ultimate processing accuracy. The 3rd type of simulations considers deposition cases, such as Cu seed layer deposition. Some results will be presented for 2D simulations and some others – for 3D simulations.

References:

[1] P. Moroz, IEEE Trans. on Plasma Science, **39** (2011) 2804.

[2] P. Moroz, D. J. Moroz, ECS Transactions, **50** (2013) 61.

[3] P. Moroz, D. J. Moroz, J. Physics: CS **550** (2014) 012030.

Surface Science
Room 104E - Session SS+AS-WeM

Environmental Interfaces, Ambient Surfaces, and In-Operando Studies

Moderator: R. Scott Smith, Pacific Northwest National Laboratory

8:00am **SS+AS-WeM1 In-situ Electron Microscopy of Synthesis, Chemistry and Self-assembly of Colloidal Nanostructures**, ***Eli Sutter,*** University of Nebraska - Lincoln **INVITED**

In-situ microscopy, particularly real-time imaging of dynamic processes has developed into an active field of research and is expected to be one of the key enabling techniques for understanding the formation of nanostructures, catalytic reactions, phase transformations, self-assembly, and other central issues in nanoscience and technology. *In-situ* transmission electron microscopy can be used to follow the behavior and measure the properties of nanostructures over a wide range of environmental conditions with resolution down to the atomic scale. While processes at variable temperatures and gas-solid interactions have been accessible for some time, observations in liquids have emerged only in recent years with the development of special membrane cells. Liquid-cell electron microscopy has developed into a powerful technique that allows the imaging of various processes in wet environments, such as liquids, solutions, or colloidal suspensions, and the investigation not only of a wide range of inorganic nanoscale objects but of biological systems as well.

I will illustrate the power of liquid-cell electron microscopy applied to imaging colloidal synthesis (nanoparticles, core-shell structure), electrochemistry (galvanic replacement reactions) and the self-assembly of nanocrystal superstructures in solution. Our results demonstrate that real-time electron microscopy can substantially advance our understanding of a wide range of processes involving nanoscale objects in bulk liquids.

8:40am **SS+AS-WeM3 Low Energy Electron Microscopy at Near Ambient Pressures**, ***Andreas Thissen,*** SPECS Surface Nano Analysis GmbH, Germany

Low-energy electron microscopy (LEEM) is a spectromicroscopy technique, which allows the study of dynamic processes at surfaces and interfaces, such as thin-film growth, surface reactions, and phase transitions. With the FE-LEEM P90 from SPECS, which is based on the instrument design by Rudolf Tromp from IBM [1,2], lateral and energy resolution of below 5 nm and 250 meV, respectively, can be achieved. Depending on the excitation source and the settings on the instrument a variety of different imaging modes are possible: mirror electron microscopy, low energy electron diffraction (LEED), phase contrast imaging, reflectivity contrast, dark field imaging and bright field imaging, as well as photoelectron emission microscopy and spectroscopy.

We have enhanced the technical capabilities of the FE-LEEM P90 towards studies under near ambient conditions by developing a special sample geometry. This enables the analysis of materials and devices under near ambient conditions and even in situ during operation.

9:00am **SS+AS-WeM4 Probing Liquid-Vapor Interfaces of Ionic Solutions with Lab-based APXPS**, ***John Newberg***, *C. Arble, Y. Khalifa, A. Broderick, S. Rani,* University of Delaware

Ionic interfaces are ubiquitous in physical, chemical, biological, environmental and technological processes. Herein we will present recent efforts examining ionic liquid and deliquescent salt interfaces using lab-based ambient pressure X-ray photoelectron spectroscopy (APXPS) in the presence of water vapor. The onset to water uptake into the top few nm of a hydrophilic ionic liquid is surprisingly similar to hydrophilic solid surfaces. A hydrophilic salt zinc bromide was also probed as it transitions from a solid to a liquid. It will be shown for ionic solutions that the uptake of water leads to variable shifts in the binding energy of anion and cation moieties driven by their interaction with water.

9:20am **SS+AS-WeM5 Effect of Surface Passivation on Stability of Methylammonium Lead Iodide Perovskite**, *Q. Peng,* ***Xiaozhou(Joe) Yu,*** University of Alabama

Methylammonium Lead Iodide Perovskite ($MAPbI_3$) is a promising photoelectronic material for various applications. However, the stability of $MAPbI_3$ is a big concern for its applications in outdoor application environments. Its stability is affected the interfaces between $MAPbI_3$ and other layers of materials, temperature, moisture, and O_2. Currently the detail decomposition mechanism is not clear yet. In this presentation, we will employ a suite of in-situ characterization methods including in-situ Fourier Transform Infrared spectrometer, quartz crystal microbalance, and quadrupole mass spectrometer to understand the decomposition mechanism when expense $MAPbI_3$ to different simulated application environments (such as Fig. 1). The effect of various surface passivation methods on the stability of $MAPbI_3$ will be presented to help illustrate the mechanism that govern the stability of $MAPbI_3$.

9:40am **SS+AS-WeM6 STM Reveals the Formation of Near-Ideal Self Assembled Monolayers on TiO_2 in Air and Solution**, ***William DeBenedetti,*** *M.A. Hines, E.S. Skibinski, A. Song, A. Ortoll-Bloch,* Cornell University

The surface chemistry of TiO_2 in air and solution is an important, but under-studied, topic for next-generation photovoltaics, environmental remediation, and CO_2 photoreduction. Using scanning tunneling microscopy (STM), polarized infrared spectroscopy and other techniques, we will show that surprisingly stable, near-ideal organic monolayers spontaneously form on rutile (110) in a variety of environments.

First, we will show that under ambient conditions, the rutile (110) surface is terminated by a monolayer of bicarbonate, HCO_3, and H formed from the reactive adsorption of CO_2 and H_2O — a reaction that has never been observed in ultrahigh vacuum. Contrary to conventional wisdom, this bicarbonate monolayer displaces H_2O bound to the surface, remaining intact even in vacuum up to ~700 K. The spontaneous formation of a HCO_3 monolayer has important implications for the mechanism of CO_2 photoreduction on TiO_2.

Second, we will show that near-ideal organic monolayers form when rutile (110) is immersed in a variety of aqueous solutions. As an example, highly ordered benzoate monolayers with a characteristic “paired” geometry can be formed from aqueous solutions. Using polarized infrared spectroscopy, we show that this pairing is not due to dimerization, as suggested by previous researchers. Instead, DFT simulations confirm that π-π interactions lead to long-range ordering and a tetrameric bonding geometry. The structure of these monolayers is further confirmed by disrupting the π-π interactions using a variety of fluoro-substituted precursors.

11:00am **SS+AS-WeM10 Study of the Electrical Double Layer of Calcium Carbonate Minerals**, ***Yijue Diao,*** *R.M. Espinosa-Marzal,* University of Illinois at Urbana-Champaign

Understanding the interactions taking place at the calcite-solution interface is crucial to elucidate many natural geochemical processes on or near the

Earth's surface, such as biomineralization and CO_2 sequestration capture of inorganic contaminants by minerals, and enhanced oil recovery. Being the most stable crystalline phase of calcium carbonate, and one of the most abundant minerals, calcite has been studied intensively at the microscale. However, when it comes to the nanoscale, little is known about the molecular details of the calcite-solution interface. Not until recently have experimental and computational works, including our previous force spectroscopy studies, shown that unlike the conventional model of Stern layer, the calcite interface in aqueous phase is well defined by two layers of water molecules on top of which loosely bound hydrated calcium ions are located. Our previous work by colloidal probe atomic force microscopy (AFM) reveals the influence of confinement on the calcite surface under equilibrium conditions.

In this study, AFM with both a microsphere and a sharp tip is employed to perturb the electrical double layer (EDL) of calcite. By performing force measurements with a short interval that does not allow the EDL reaching equilibrium between consecutive force measurements, we perturb the EDL and afterwards scrutinize the kinetics of EDL re-formation. It has been shown that the calcite interface can be tuned by varying calcium concentration and hence, the influence of calcium concentration on the kinetics of EDL formation is also studied. On the other hand, we directly probe into the behavior of the Stern layer by resolving the film thickness transitions (FTTs) that result from squeezing-out layers of molecules confined between the tip and calcite. The significant difference in the confined area, which therefore induces confinements of different extent between the colloidal probe and the sharp tip, allow understanding the influence of the confinement on the EDL.

Calcium carbonate is stored in nanopores of marine organisms and of rocks. Knowing the nanoconfined interfacial structure of calcite from our previous study, we take one step further in this work to investigate the kinetics of the EDL formation under the perturbation induced by consecutive confinement, which allows us not only to spatially elucidate the calcite-solution interface, but also with time resolution.

11:20am **SS+AS-WeM11 Observation of Water Adsorption Structures on Ultrathin ZnO/Au(111)**, ***Junseok Lee***, *D.C. Sorescu, X. Deng,* National Energy Technology Laboratory

Adsorption of water at the nanostructured metal oxide surfaces has implications in catalysis and serves as a prototypical system in studying water-oxide interfaces. In this work, the adsorption of water on ultrathin ZnO nanostructures grown on Au(111) substrate is investigated using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. Water overlayers are grown on well-defined monolayer and bilayer of ZnO nanostructures. STM images of water overlayer structures on the monolayer and the bilayer of ZnO nanostructures at low temperature are analyzed in detail at different water coverages with the help of DFT calculation results. Moire pattern is found to influence the adsorption structure of water on the ZnO nanostructure surfaces and the brightness of the Moire pattern of the ZnO structure is observed to be significantly modulated by the adsorption of water molecule. Various hydrogen bonded water network structures are observed on ZnO bilayer after desorbing excess water molecules. The edge of the ZnO monolayer is found to be decorated by water molecules up to room temperature but there was no evidence of adsorption of water at the edge of ZnO bilayer.

11:40am **SS+AS-WeM12 Surface and Bulk Crystallization Kinetics of Amorphous Solid Water Nanoscale Films**, ***Chunqing Yuan***, *R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

We investigate the crystallization kinetics of nanoscale amorphous solid water (ASW) films using temperature-programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). ASW is a metastable form of water created by vapor deposition on a cold substrate ($T<130$ K). We directly measure the surface (using TPD) and bulk (using RAIRS) ASW crystallization kinetics as a function of film thickness and temperature. The results show that nucleation and crystallization begins at the ASW/vacuum interface and then the crystallization growth front propagates linearly into the bulk. The linear propagation is further confirmed by adding a thin layer of isotopic D_2O ice indicator at different positions in the ice. These results show that the closer the isotopic layer is to the vacuum interface, the sooner the isotopic layer crystalizes, which confirms the top-down propagation of the crystallization front. Further evidence for ASW/vacuum interface nucleation mechanism comes from experiments where a decane layer is deposited on top of the ASW film. The presence of the decane layer impedes surface nucleation and dramatically decreases the crystallization rate. By separating surface nucleation and bulk propagation processes, we are able to extract the nucleation and growth rates of ASW crystallization between 140-160 K.

This work was supported by the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. The research was performed using EMSL, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated by Battelle operated for the DOE.

12:00pm **SS+AS-WeM13 Capture of Hyperthermal Atoms and Molecules by Amorphous Water Ice via Ballistic Embedding**, ***Grant Langlois***[*][†], *S.J. Sibener,* University of Chicago

We present comprehensive work detailing the capture and aggregation of hyperthermal atoms and molecules (CO_2, CF_4, Xe, Kr) by amorphous solid water (ASW) under ultra-high vacuum conditions at 125 K, near the amorphous/crystalline transition. Using time-resolved *in situ* reflection-absorption infrared spectroscopy (RAIRS), the gases prepared in supersonic molecular beams with translational energies above ~3.0 eV are observed to directly embed underneath the vacuum-ice interface to become absorbed within amorphous ice films despite an inability to adsorb at 125 K. Embedding into crystalline films, when observed, is less effective. Upon embedding, resultant mobility within the ice and the strength of intermolecular interactions can yield segregation of these gases into clusters, as seen in the case of CO_2. Tracing the kinetics of these embedding events under different energetic conditions allows for elucidation of the underlying dynamics, and we draw comparison between all studied gases to promote generalized conclusions in regards to empirical prediction of embedding probability. Through application of a classical model of the entrance barrier for atoms and molecules colliding with amorphous ice, we provide direct evidence for a unified connection between embedding probability and momentum of the incoming atoms and molecules; an account of all embedding data measured by our group traces a singular barrier. This work highlights the interplay between translational energy and momentum accommodation during collisions with ice; atoms and molecules can become trapped in an icy surface despite an inability to simply stick to the interface. These results are of considerable importance to studies of both the astrochemistry and evolution of interstellar bodies and dust, and detailing the capture and release of gases by permafrost relating to global climate forcing.

---

[*] **Morton S. Traum Award Finalist**

[†] **National Student Award Finalist**

Electronic Materials and Photonics
Room 102A - Session EM+NS+SP+SS-WeA

Nanoscale Imaging of Metals and Compound Semiconductor based Nanostructures, Surfaces and Interfaces

Moderators: Yohannes Abate, Georgia State University, Andy Antonelli, Nanometrics

2:20pm **EM+NS+SP+SS-WeA1 The Importance of Contact Engineering for 2D Devices***, **Saptarshi Das**,* Pennsylvania State University **INVITED**

Contact resistance is one of the most important factors which could potentially limit the performance of novel electronic and optoelectronic devices based on two-dimensional (2D) materials like graphene, black phosphorus, various transition metal dichalcogenides (TMDs) like MoS_2, WSe_2 and beyond [1-3]. It is now widely accepted that metal-2D contacts are mostly Schottky barriers type [1-3]. Hence, various contact engineering strategies have been adopted to minimize the Schottky barrier height at the metal-2D interface and thereby reduce the contact resistance. In this talk I will provide a comprehensive overview of different contact engineering schemes metal work function engineering, interface engineering and phase engineering [4-6]. Additionally, I will also talk about the scalability of the contact resistance since an aggressively scaled 2D device will also have aggressively scaled contacts.

1. Das S, Chen H-Y, Penumatcha AV, Appenzeller J: **High performance multilayer MoS2 transistors with scandium contacts**. *Nano letters* 2012, **13**(1):100-105

2. Das S, Appenzeller J: **WSe2 field effect transistors with enhanced ambipolar characteristics**. *Applied Physics Letters* 2013, **103**(10):103501

3. Das S, Demarteau M, Roelofs A: **Ambipolar phosphorene field effect transistor**. *ACS nano* 2014, **8**(11):11730-11738.

4. Das S, Appenzeller J: **Where does the current flow in two-dimensional layered systems?***Nano letters* 2013, **13**(7):3396-3402

5. Das S, Gulotty R, Sumant AV, Roelofs A: **All two-dimensional, flexible, transparent, and thinnest thin film transistor**. *Nano letters* 2014, **14**(5):2861-2866.

6. Kappera R, Voiry D, Yalcin SE, Branch B, Gupta G, Mohite AD, Chhowalla M: **Phase-engineered low-resistance contacts for ultrathin MoS2 transistors**. *Nature materials* 2014, **13**(12):1128-1134.

3:00pm **EM+NS+SP+SS-WeA3 Imaging Stress-Directed Compositional Patterning in Silicon Germanium with μ-Raman Spectroscopy***, **Brian Rummel**, 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 an epitaxial compound semiconductor film.[1] This compositional patterning laterally manipulates quantum barriers within the film in a press-and-print manner. In this example, an array of silicon pillars is pressed against a relaxed $Si_{0.8}Ge_{0.2}$ substrate in a mechanical press, and the entire assembly is heated to high temperatures. This serves to promote a diffusive separation of the germanium into highly localized regions. Here, the difficulty in analyzing these structures is due to the lack of surface detail on the stress-annealed substrate as there is only elastic deformation observed during the fabrication process. To visualize the regions compressively stressed by the pillars and therefore compositionally altered regions, we report the use of μ-Raman spectroscopy to produce a 2D compositional map of a substrate. The substrate is patterned with feature sizes on the order of 1 to 3 microns to remain within the spatial resolution of μ-Raman spectroscopy for the purpose of demonstration. The first-order Raman spectrum for pure silicon and germanium produces peaks at 520.2 and 300.7 cm^{-1}, respectively. The deviations from these relaxed silicon and germanium peaks have been attributed to residual tensile stress in the Ge-depleted regions. Lateral line scans are performed to map the compositions of the stressed and annealed substrate, which provides a clear image of the resulting diffusion process. This imaging also allows the quantum structures to be addressable.

[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," *Applied Physic Letters* **107,** 072106-1:5 (2015).

3:20pm **EM+NS+SP+SS-WeA4 Atomic-scale Characterization of III-V Nanowire Heterostructures and Devices***, J. Knutsson, S. McKibbin, M. Hjort, J. Colvin, S. Yngman, A. Troian, O. Persson, A. Mikkelsen, **Rainer Timm**,* Lund University, Sweden

III-V semiconductor nanowires (NWs) have a large technological potential within electronics, optoelectronics, and energy harvesting [1]. With their flexibility in creating heterostructures, by radial and axial stacking during epitaxial growth, comes an increasing complexity of device structure. Furthermore, due to their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly determined by surface properties. It is therefore essential to study the structural and electronic properties of NW surfaces down to the atomic level and across interfaces regarding doping, material composition, or crystal phase.

We recently obtained atomically resolved scanning tunneling microscopy (STM) images of various GaAs, InAs, and InP NW surfaces [2,3]. By combining STM imaging with scanning tunneling spectroscopy (STS) measurements, we correlate the surface structure and local electronic properties [3]. Here, we will present examples from InAs NWs with interfaces between different crystal phase. Our low-temperature STM/S results show that even the smallest possible insertion of zincblende phase within a wurtzite segment, a single bilayer stacking fault, shows a clear zincblende signature. We observe transitions in the local density of states with sub-nm lateral resolution. Furthermore, we map the interface band alignment and measure quantum confinement energies of single and double bilayer stacking faults.

Beyond traditional steady-state surface characterization, it is desirable to even investigate nanostructure devices *in-situ*, meaning while they are operating under an applied bias. We are now using simultaneous STM, AFM, and electrical transport measurements for studying individually contacted NWs during device operation [4], complemented by Kelvin probe force microscopy and scanning photoemission microscopy. We will present initial results of such combined *in-situ* studies on axial *pn*-junctions in InP and GaInP NWs, where we also investigate the influence of NW surface modification (e.g. removal of native oxide by atomic hydrogen) on photovoltaic properties.

[1] E. Lind *et al.,* IEEE J. El. Dev. Soc. **3**, 96 (2015); J. Wallentin *et al*., Science **339**, 1057 (2013).

[2] M. Hjort *et al*., ACS Nano **6**, 9679 (2012); J. Knutsson *et al.,* ACS Appl. Mat. & Interf. **7**, 5748 (2015).

[3] M. Hjort *et al*., Nano Lett. **13**, 4492 (2013); M. Hjort *et al.,* ACS Nano **8**, 12346 (2014).

[4] O. Persson *et al.,* Nano Lett. **15**, 3684 (2015); J. L. Webb *et al*., Nano Res. **7**, 877 (2014).

4:20pm **EM+NS+SP+SS-WeA7 Revealing Optical Properties of Reduced-Dimensionality Materials at Relevant Length Scales using Nanospectroscopic Imaging***, **P. James Schuck**,* The Molecular Foundry, Berkeley Lab **INVITED**

Reduced-dimensionality materials for photonic and optoelectronic applications including energy conversion, solid-state lighting, sensing, and information technology are undergoing rapid development. The search for novel materials based on reduced-dimensionality is driven by new physics. Understanding and optimizing material properties requires characterization at the relevant length scale, which is often below the diffraction limit. The nano-optical imaging community has now crossed the boundary from insufficient to sufficient resolution, mapping critical optoelectronic properties in these exciting materials at their native length scales. Here, I will describe the recent near-field imaging advances that lay groundwork for generally-applicable nano-optical studies of these low-D materials, and will show recent results on 0, 1, and 2D systems. I will spend time discussing the importance of near-field polarization in probing these materials, and will also highlight recent applications in 2-D semiconductor transition metal dichalcogenides (TMDCs), where we and others have uncovered new optoelectronic regions and spatially-varying features that were hidden in prior optical studies. These findings have broad implications for the development of atomically thin transistors, quantum optical components, photodetectors and light-emitting devices.

5:00pm **EM+NS+SP+SS-WeA9 Polarizability Mapping of Nanolayers Based on Near-Field Edge Fringes***, **Viktoriia Babicheva**, V.S. Yakovlev, S. Gamage, M.I. Stockman, Y. Abate,* Georgia State University

Scattering-type scanning near-field optical (s-SNOM) microscopy enable spectroscopic imaging with nanoscale resolution and provide chemical and structural information of surfaces [1]. In this work, we investigate identification of material type using an approach based on analyzing near fields at the sample edge [2]. We develop theoretical approach that includes full-wave numerical simulations and calculations of s-SNOM signal in different demodulation orders. This model allow characterization of structures of any shape and material, as well as different tips, and does not include any fitting parameters. In this way, we defined that metallic edge has bright and dark fringes in near-field characterization, whereas a bright edge of dielectric material has no outside fringe. Similar behavior is observed for anisotropic material with hyperbolic dispersion (boron nitride in mid-IR range): depending on the wavelength, it shows either metallic or dielectric properties.

1. Y. Abate, R.E. Marvel, J.I. Ziegler, S. Gamage, M.H. Javani, M.I. Stockman, and R.F. Haglund "Control of plasmonic nanoantennas by reversible metal-insulator transition" Sci. Rep. 5, 13997 (2015).

2. Y. Abate, S. Gamage, L. Zhen, S.B. Cronin, H. Wang, V. Babicheva, M.H. Javani, M.I. Stockman, "Nanoscopy reveals metallic black phosphorus," Light: Science & Applications, accepted (2016). http://arxiv.org/abs/1506.05431

5:20pm **EM+NS+SP+SS-WeA10 Wedding Cake Growth Mechanism in One-Dimensional and Two-Dimensional Nanostructure Evolution***, Xin Yin*[*]*,* University of Wisconsin-Madison*; J. Shi,* Rensselaer Polytechnic Institute*; X. Niu,* Northeastern University*; D. Geng,* University of Wisconsin-Madison*; H. Huang,* Northeastern University*; X.D. Wang,* University of Wisconsin-Madison

Morphology is one essential element that gives rise to extraordinary physical, chemical, and mechanical properties in nanomaterials. Precise morphology control of nanomaterials is a notorious task, which heavily relies on fundamental understanding of the governing atomistic mechanisms and kinetics at the nanoscale. Despite numerous studies on the growth and application of nanostructures, current understanding of kinetics that governs the nanocrystal evolution is yet limited.

By programming deposition conditions at time domain, we observed the wedding cake growth mechanism in the formation of 2D ZnO nanostructures. Within a narrow growth window, the surfaces of 2D structures were covered with a unique concentric terrace feature. This mechanism was further validated by comparing the characteristic growth rates to the screw dislocation-driven model. An interesting 1D to 2D morphology transition was also found during the wedding cake growth, when the adatoms overcome the Ehrlich-Schwoebel (ES) barrier along the edge of the top crystal facet triggered by lowering the supersaturation. The evolution of 2D plate structure from 1D pillars represents a dynamic crystal growth behavior transition when the local deposition conditions were tuned in-situ. It lively recorded the wedding cake growth model in nanostructure formation from vapor phase, which was rare to be observed when the deposition conditions were remained constant. The terrace feature on these nanostructures provided a valuable platform for understanding the wedding cake growth kinetics that could be an important mechanism to design and predict the nanocrystal morphology formation from the bottom-up. Analyzing the supersaturation and temperature-related growth behavior provides a new insight into nanostructure growth mechanisms and morphology control.

Wedding cake growth is a layer-by-layer growth model commonly observed in epitaxial growth of metal films, featured by repeated nucleation of new atomic layers on the topmost surface owing to the confinement of the Ehrlich–Schwoebel (ES) barrier. This study expands the application of the wedding cake growth mechanism to the nanostructure growth. It enriches our understanding on the fundamental kinetics of nanostructured crystal growth and provides a transformative strategy to achieve rational design and control of nanoscale geometry.

5:40pm **EM+NS+SP+SS-WeA11 Detecting the Invisible - The Atomic Structure of Radiation Sensitive Nano-Materials***, **Christian Kisielowski**,* Molecular Foundry, Lawrence Berkeley National Laboratory*; P. Specht,* University of California Berkeley **INVITED**

As heterogeneous materials scale below 10 nm, a suitable combination of single digit nanocrystals with their rich variety of tunable surfaces and interfaces allows tailoring unprecedented materials with novel structure-function relationships. The design of new catalysts [1], investigations of polymers at atomic resolution [2] or analyses of deviations from a random doping distributions at atomic resolution [3] may serve as examples. This contribution describes research that aims at exploiting the emerging ability to analyze and understand such materials by directly determining their atom arrangement in three-dimensions using aberration-corrected transmission electron microscopy [4]. Attempts to unravel the atomic structure of such nanoscale composites in this manner must explicitly address their pronounced sensitivity to the probing radiation that can unintentionally alter their pristine structure, often beyond recognition. We address this challenge by applying low dose-rate in-line holography [5], which allows operating electron microscopes with dose rates as low as 5-10 e/Å²s that help maintaining structural integrity at atomic resolution to an unexplored end. The approach mimics best practices in biological research but achieves atomic resolution with single atom sensitivity by the acquisition of large image series. We observe a variety of previously unknown atom configurations in surface proximity of CoO_x nanocrystals and coatings that are hidden behind unusually broadened diffraction patterns but become visible in real space images because the phase problem is solved. The observed structures are drastically altered by an exposure of the material to water vapor or other gases, which is investigated at atomic resolution in environmental electron microscopy. It is shown for Rh/W catalysts that electron beam-induced atom dynamics can be entirely suppressed even for atom clusters made from less than 10 atoms. Resultantly, chemical compositions can be determined by contrast measurements alone and functional processes can be triggered and tracked in real time at atomic resolution.[6]

[1] J. A. Haber et al., **Advanced Energy Materials** 5 (2015) 1402307

[2] D. Lolla et al., **Nanoscale** 8 (2016) 120 - 128

[3] P. Specht, C. Kisielowski, On the chemical homogeneity of InxGa1-xN alloys - Electron microscopy at the edge of technical limits, submitted (2016)

[4] F.R. Chen et al., **Nature Commun**. 7:10603 doi: 10.1038/ ncomms10603 (2016)

[5] C. Kisielowski, **Advanced Materials** 27 (2015) 5838-5844

[6] The Molecular Foundry, which is supported by the Office of Science, the Office of Basic Energy Sciences, the U.S. Department of Energy under Contract No. DE-AC02-05CH11231

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 103A - Session HC+NS+SS-WeA
Nanoscale Surface Structures in Heterogeneously Catalyzed Reactions

Moderator: Arthur Utz, Tufts University

2:20pm **HC+NS+SS-WeA1 Ceria Nanoclusters on Graphene/Ru(0001): A New Model Catalyst System***, Z. Novotny,* Pacific Northwest National Laboratory*; F.P. Netzer,* Karl-Franzens University, Austria*; **Zdenek Dohnalek**,* Pacific Northwest National Laboratory **INVITED**

Cerium oxide is an important catalytic material known for its ability to store and release oxygen, and as such, it has been used in a range of applications, both as an active catalyst and as a catalyst support. Using scanning tunneling microscopy and Auger electron spectroscopy, we investigated the growth of ceria nanoclusters and their oxygen storage/release properties on single-layer graphene (Gr) on Ru(0001) with a view towards fabricating a stable system for model catalysis studies. The ceria nanoclusters are of the CeO_2(111)-type and are anchored at the intrinsic defects of the Gr surface and display a remarkable stability against reduction in ultrahigh vacuum up to 900 K, but some sintering of clusters is observed for temperatures > 450 K. The evolution of the cluster size distribution suggests that the sintering proceeds via a Smoluchowski ripening mechanism, i.e. diffusion and aggregation of entire clusters. To follow the cluster redox properties we examined their oxygen storage and release in an oxygen atmosphere ($<10^{-6}$ Torr) at elevated temperature (550 – 700 K). Under oxidizing conditions, oxygen intercalation under the Gr layer is observed. Time dependent studies demonstrate that the intercalation starts in the vicinity of the CeO_x clusters and extends until a completely intercalated layer is observed. Atomically resolved images further show that oxygen forms a p(2×1) structure underneath the Gr monolayer. Temperature dependent studies yield an apparent kinetic barrier for the intercalation of 1.2 eV. At higher temperatures, the intercalation is followed by a slower etching of the intercalated Gr (apparent barrier of 1.6 eV). Vacuum annealing of the intercalated Gr leads to the formation of carbon monoxide and causing etching of the Gr film thus revealing that the spillover of oxygen is not reversible. These studies

---

[*] **NSTD Student Award Finalist**

demonstrate that the easily reducible CeO_x clusters act as intercalation gateways capable of efficiently delivering oxygen underneath the Gr layer.

3:00pm **HC+NS+SS-WeA3 Lowering the Barrier to C-H Activation using Pt/Cu Single Atom Alloys**, ***Matthew Marcinkowski***, *M. El Soda, F.R. Lucci, E.C.H. Sykes,* Tufts University

Due to the increased in shale gas production in recent years the availability of light alkanes such as ethane and propane has increased significantly. Although these chemicals are typically considered inert, the ability to cleave C-H bonds in alkanes would allow for production of alkenes, which are important precursors to polymers. In this work, we use a surface science approach to model C-H activation on a Cu(111) surface using methyl iodide. Methyl iodide is known to decompose to produce methyl groups and iodine atoms on Cu(111) below 200 K. The methyl groups are then stable on the surface up until 450 K, at which temperature they decompose to form a number of products including methane, ethylene, ethane, and propylene. The rate limiting step to forming these products is the activation of one of the C-H bonds in the methyl group to produce surface bound hydrogen and methylene. Pt(111) is also able to activate the C-I bond in methyl iodide, but methyl groups on this surface only produce methane, hydrogen, and surface bound methylene groups at 290 K. While the barrier to C-H activation is lowered on Pt compared to Cu, the Pt surface is unable to perform carbon coupling reactions. Inspired by these previous results, we fabricated surfaces consisting of 1% Pt in the Cu(111) surface. At this concentration, Pt exists as single, isolated atoms substituted into the Cu(111) lattice. These *single atom alloys* exhibit synergistic chemistry and yield the desirable properties of each of the two pure metal surfaces. They are able to produce carbon coupling products like pure Cu, but are able to activate the C-H bond necessary to begin these reactions at 340; 110 K cooler than on Cu(111). Increasing the concentration of Pt further decreases the temperature necessary to activate C-H bonds, but also decreases the amount of carbon coupling products formed as the surface becomes more similar to Pt(111). Single atom alloys therefore provide an ideal model catalyst for the decomposition of methyl iodide, allowing for more facile activation of the C-H bond than pure Cu while also producing the desired coupling products, which Pt(111) is unable to do.

3:20pm **HC+NS+SS-WeA4 Formation, Migration and Reactivity of Au-CO Complexes on Gold-Surfaces**, ***Jun Wang***, Oak Ridge National Laboratory; *M. McEntee, W. Tang, M. Neurock,* University of Virginia; *A.P. Baddorf, P. Maksymovych,* Oak Ridge National Laboratory; *J.T. Yates, Jr.,* University of Virginia

We report experimental as well as theoretical evidence that suggests formation of Au-CO complexes upon the exposure of CO to active sites (step edges and threading dislocations) on a Au(111) surface. Room-temperature scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy, transmission infrared spectroscopy, and density functional theory calculations point were combined to investigate morphological changes of the Au(111) surface with an intentionally created array of etch-pits. Room-temperature STM of the Au(111) surface at CO pressures in the range from 10^{-8} to 10^{-4} Torr (dosage up to 10^6 langmuir) indicates Au atom extraction from dislocation sites of the herringbone reconstruction, mobile Au–CO complex formation and diffusion, and Au adatom cluster formation on both elbows and step edges on the Au surface. The formation and mobility of the Au–CO complex result from the reduced Au–Au bonding at elbows and step edges leading to stronger Au–CO bonding and to the formation of a more positively charged CO ($CO^{\delta+}$) on Au. Our studies indicate that the mobile Au–CO complex is involved in the Au nanoparticle formation and reactivity, and that the positive charge on CO increases due to the stronger adsorption of CO at Au sites with lower coordination numbers.

ACKNOWLEDGEMENTS: Part of this research was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility .

Reference: J. Wang, M. McEntee, W. Tang, M. Neurock, A. P. Baddorf, P. Maksymovych, and J. T. Yates, Jr., *J. Am. Chem. Soc.* 138, 1518 (2016)

4:20pm **HC+NS+SS-WeA7 Sulfur-Metal Complexes on Surfaces of Copper, Silver, and Gold**, ***Patricia A. Thiel,*** Iowa State University; *H. Walen,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan; *D.-J. Liu,* Ames Laboratory, Ames, IA; *J. Oh,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan; *H.J. Yang,* University College London, UK; *Y. Kim,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan **INVITED**

The nature of sulfur interaction with surfaces of coinage metals (M=Cu, Ag, Au) is relevant to aspects of heterogeneous catalysis, corrosion, and self-assembled monolayers. We have discovered a number of unexpected complexes—independent, molecule-like MxSy species—that form on low-index M surfaces. In a sense, these complexes are iidway between the well-known phenomena of chemisorption and adsorbate-induced reconstruction. Our primary experimental tool is scanning tunneling microscopy (STM) used in ultrahigh vacuum. We tailor our experimental conditions to isolate the complexes, by working at ultra-low sulfur coverage to avoid competition from surface reconstructions. Furthermore, we prepare the surface at 300 K, but image at 5 K, in order to immobilize these small species. Density fucntional theory (DFT) is used to interpret the experimental results. For instance, application of DFT is essential to identify the complexes that form on Cu(111), Ag(111), and Au(100), and this identification is made both on the basis of their physical characteristics in real vs. stiimulated STM images (size, orientation, shape) as well as their calculated stability. On other surfaces, including Au(111), Cu(10o0), and Au(110), MxSy complexes do not form under comparable conditions. This broad database and extensive analysis provides insights into factors that favor complexation in this class of systems.

5:00pm **HC+NS+SS-WeA9 Titania/Gold Inverse Model Catalysts for Acetaldehyde Formation from Ethanol**, ***Ashleigh Baber***, *D.T. Boyle, W. Andahazy, V. Lam, D. Schlosser, N. Tosti, J. Wilke,* James Madison University

The fundamental investigation of the catalytic chemistry of ethanol at interfaces is important for many fields including the automotive industry due to the use of ethanol as a fuel. The redox chemistry of small alcohols, including methanol and propanol, has been studied on Au(111) supported TiO_2 nanoparticles, yet the active site for the chemistry has not yet been elucidated. Here, the systematic study of ethanol has been investigated on Au(111) and TiO_2/Au(111) via temperature programmed desorption in an effort to gain insight on the interfacial role of the reactivity for ethanol, as a function of titania coverage. Ex situ atomic force microscopy was used to image the gold–supported titania particles, and X-ray photoelectron spectroscopy was used to confirm the presence of titania on the surface. The presence of TiO_2 nanoparticles on Au(111), ~25 nm in diameter, led to the catalytic conversion of ethanol to acetaldehyde at temperatures greater than 400 K. The interaction of ethanol with Au(111)–supported TiO_2 nanoparticles is markedly different than its interaction with the individual counterparts: bulk titania and gold, which both lead to the desorption of molecular ethanol at temperatures lower than 400 K.

5:20pm **HC+NS+SS-WeA10 Shape and Support Interaction of Size Selected Pt Nanoparticles in Presence of H_2**, ***Mahdi Ahmadi***, *F. Behafarid,* University of Central Florida; *B. Roldan Cuenya,* Ruhr-University Bochum, Germany

Pt nanoparticles (NPs) supported on TiO2 have been widely used as a catalysts in industrial applications.

Strong metal-support interaction (SMSI) is expected to occur for this system under reducing environments

such as vacuum and H2. Since the morphology of NPs depends on their surface energy and their interaction

with the support, investigating the shape of NPs could be an excellent pathway to understand the metal

support interactions. In this study we have investigated the in situ shape evolution of TiO2 supported Pt NP

using grazing incidence small angle X-ray scattering (GISAXS) during annealing in H2 environment. The

size selected Pt NPs with an initial spherical shape were synthesized via inverse micelle encapsulation

method. The sample was step annealed up to 700°C in H2 environment and the onset for NPs faceting was

found to be 600°C. Annealing at a higher temperature (700°C) did not cause any further change in NPs

structure. The presence of a sharp scattering ray at 45° with respect to the surface normal indicates the (110) facet to be the dominant side facet for Pt NPs and the top and interfacial facets to be Pt(100). These features

point out that the shape of Pt NPs supported on TiO2 under hydrogen environments is pyramidal. The

specific shape of Pt NPs are discussed based on the SMSI phenomenon.

5:40pm **HC+NS+SS-WeA11 Single Atom Alloys as a Strategy for Selective Heterogeneous Hydrogenation and Dehydrogenation Reactions*, Charles Sykes,*** Tufts University **INVITED**

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 demonstratedhow single palladium and palladium atoms can convert the otherwise catalytically inert surface of an inexpensive metal into an ultraselective catalyst.(1-3) 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. Platinum/copper nanoparticles can perform the industrially important butadiene hydrogenation at lower temperature using just 1% platinum.(3) 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.*

References:

1) G. Kyriakou, M. B. Boucher, A. D. Jewell, E. A. Lewis, T. J. Lawton, A. E. Baber, H. L. Tierney, M. Flytzani-Stephanopoulos and E. C. H. Sykes – **Science** 2012, 335, 1209

2) M. D. Marcinkowski, A. D. Jewell, M. Stamatakis, M. B. Boucher, E. A. Lewis, C. J. Murphy, G. Kyriakou and E. C. H. Sykes - **Nature Materials** 2013, 12, 523

3) F. R. Lucci, J. Liu, M. D. Marcinkowski, M. Yang, L. F. Allard, M. Flytzani-Stephanopoulos, and E. C. H. Sykes - **Nature Communications** 2015, 6, 8550

Surface Science
Room 104D - Session SS+AS+EM-WeA

Semiconductor Surfaces and Interfaces

Moderator: Andrew Gellman, Carnegie Mellon University

2:20pm **SS+AS+EM-WeA1 Adsorption of Triethylenediamine on Si(100)-2×1 Surface via N-Si Dative Bonding and C-N Dissociation*, Jing Zhao,*** *M. Madachik,* University of Delaware*; K. O'Donnell,* Curtin University, Australia*; O. Warschkow,* University of Sydney, Australia*; L. Thomsen,* Australian Synchrotron, Australia*; G. Moore, S. Schofield,* University College London*; A.V. Teplyakov,* University of Delaware

The functionalization of silicon surfaces with thin layers of organic materials is an important area of studies with current and potential applications in microelectronics, catalysis, and bio-sensing. Triethylenediamine (also known as 1,4-diazabicyclo[2.2.2]octane, or DABCO) presents an interesting case study for silicon functionalization because of its symmetric structure with two x nitrogen atoms in tertiary amine configuration. Each of these atoms could potentially form a dative bond with a clean Si(100)-2x1 surface while the other may remain accessible for further modification. We applied infrared spectroscopy (MIR-FTIR), X-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD) supported by density functional theory calculations (DFT) to investigate the reaction mechanism of triethylendiamine with a clean Si(100)-2×1 surface, focusing specifically on dative bond formation and C-N dissociation.

2:40pm **SS+AS+EM-WeA2 Chemoselective Adsorption of Functionalized Cyclooctynes on Silicon***, M. Reutzel, N. Munster, M.A. Lipponer,* Philipps-Universität Marburg, Germany*; C. Langer,* Justus Liebig University Giessen, Germany*; U. Hofer, U. Koert,* Philipps-Universität Marburg, Germany*; **Michael Durr**,* Justus Liebig University Giessen, Germany

The adsorption of organic molecules on silicon surfaces has been subject of intense research due to the potential applications of organic functionalization of silicon surfaces in semiconductor technology. The high reactivity of the silicon dangling bonds, however, presents a major hindrance for the first basic reaction step of such a functionalization, i.e., chemoselective attachment of bifunctional organic molecules on the pristine silicon surface. Due to the high reactivity of the dangling bonds, each functional group of a bifunctional molecule adsorbs with an initial sticking coefficient close to unity and thus the final adsorption product will typically consist of a mixture of molecules adsorbed via different functional groups.

We overcome this problem employing cyclooctyne as the major building block of our strategy. Using scanning tunneling microscopy and X-ray photoelectron spectroscopy, cyclooctyne derivatives with different functional side groups are shown to react on Si(001) selectively via the strained cyclooctyne triple bond while leaving the side groups intact. The origin of this chemoselectivity is traced back to the different adsorption dynamics of the functional groups involved. We show that cyclooctyne's strained triple bond is associated with a direct adsorption channel on the Si(001) surface, in contrast to most other organic molecules which adsorb via weakly bound intermediates. In these intermediate states, the molecules have a finite lifetime and are often mobile and free to rotate on the surface. This allows the bifunctional molecule to sample the surface with the strained triple bond during its finite lifetime in the trapped state and in consequence, bifunctional molecules with a strained triple bond as one functional group will end up with this group attached to Si(001) even if the initial interaction proceeds via the second functional group.

Chemoselectivity can thus be achieved even on the highly reactive Si(001) surface when exploiting the adsorption dynamics of the respective reaction channels.

3:00pm **SS+AS+EM-WeA3 Compositions, Structures, and Electronic Properties of Grain Boundaries of Cu(InGa)Se$_2$*, Xudong Xiao,*** Chinese University of Hong Kong **INVITED**

Polycrystalline semiconductors are important energy materials and the grain boundaries play crucial role in their electrical transport property. While in general grain boundary is detrimental, for Cu(InGa)Se$_2$ (CIGS), it was found that the grain boundary is benign to the electrical transport and a record solar cell energy conversion efficiency of 22.3%, the best among all thin film solar cells, has been achieved with a polycrystalline film. This peculiar benign behavior has attracted great attention in the materials science community, unfortunately, even with tremendous effort, the mechanism of the benignity of CIGS grain boundary remains as an outstanding problem, mostly due to the lack of convincing experimental evidences.

We performed our study by design and prepare well controlled CIGS samples with two different Cu content. By careful treatment of the samples to remove artifacts, we used a combination of techniques, namely AFM, STM, and TEM, to probe at nanoscales the composition, structure, and electrical properties of the individual grain boundary in direct comparison to those of the individual grain interior. We discovered that the grain boundary in fact consists of a boundary layer of finite thickness in addition to the grain boundary surface/interface for the non Σ3 grain boundaries. This boundary layer has a definitive composition, structure, and electronic band, independent of the overall Cu content in the CIGS films. The observation of similar grain interior and similar grain boundary except the boundary layer thickness for the two samples with very different overall Cu content is indeed a surprising finding that has never been reported before. The band alignment between grain boundary and grain interior was discovered to be of type II with downward offset for both conduction and valence bands at grain boundary, well correlating to the local copper deficiency and structure. Our findings expressively support the type inversion and large hole barrier in this grain boundary layer, and establish a comprehensive mechanism for the suppression of carrier recombination therein.

4:20pm **SS+AS+EM-WeA7 Thermal Self-limiting CVD Silicon and ALD Silicon Nitride Containing Control Layers on $In_{0.53}Ga_{0.47}As$(001)-(2x4), $Si_{0.5}Ge_{0.5}$(110), and $Si_{0.7}Ge_{0.3}$(001)**, ***Steven Wolf***, *M. Edmonds, T. Kent, K. Sardashti,* University of California at San Diego*; M. Chang, J. Kachian,* Applied Materials*; R. Droopad,* Texas State University*; E. Chagarov, A.C. Kummel,* University of California at San Diego

Compound semiconductors with high mobilities such as InGaAs and SiGe are being employed in metal oxide semiconductor field effect transistors (MOSFETs) to increase transistor performance. However, these surfaces contain dangling bonds that can affect the surface Fermi level; thus, depositing a control layer via ALD or self-limiting CVD on multiple materials and crystallographic faces is required . Silicon uniquely bonds strongly to all crystallographic faces of $InGa_{1-x}As$, $In_xGa_{1-x}Sb$, $In_xGa_{1-x}N$, SiGe, and Ge enabling transfer of substrate dangling bonds to silicon, which can then be passivated by atomic hydrogen. Subsequently, the surface may be functionalized with an oxidant such as HOOH in order to create a terminating Si-OH layer, or a nitriding agent such as N_2H_4 in order to create an Si-N_x diffusion barrier and surface protection layer. This study focuses on depositing saturated Si-H_x and Si-OH seed layers via a self-limiting CVD process on InGaAs(001)-(2x4), and depositing a Si-N_x seed layer on $Si_{0.5}Ge_{0.5}$(110) and $Si_{0.7}Ge_{0.3}$(001) via an ALD process. XPS in combination with STS/STM were employed to characterize the electrical and surface properties of these control layers on the various surfaces. A thin Si-H_x capping layer (2.5 monolayers) was deposited in a self-limiting CVD fashion on InGaAs(001)-(2x4) by exposing to Si_2Cl_6 at 350°C. This layer allows for multilayer silicon or Si-O_x growth by ALD through cyclically dosing Si_2Cl_6 with either atomic H or anhydrous HOOH. STM and STS measurements show the Si_2Cl_6 exposed InGaAs(001)-(2x4) surface is atomically locally ordered and has an unpinned surface Fermi level. Exposure to anhydrous HOOH at 350°C terminates the surface with Si-O bonds and does not lead to oxidation of substrate peaks. The HOOH treated surface then nucleates TMA at 250°C and ultimately further high-k gate oxide growth. MOSCAP device fabrication was performed on n-type InGaAs(001) substrates with and without a Si-H_x passivation control layer deposited by self-limiting CVD in order to determine the effects on $C_{max,}$ frequency dispersion, and midgap trap states. Deposition of a SiO_xN_y diffusion barrier and surface protection layer was achieved on the $Si_{0.5}Ge_{0.5}$(110) and $Si_{0.7}Ge_{0.3}$(001) surfaces via an ALD process at 275°C through cyclically dosing Si_2Cl_6 and anhydrous N_2H_4. MOSCAP device fabrication was performed on $Si_{0.7}Ge_{0.3}$(001) with and without a SiO_xN_y passivation control layer to compare device performance. Ultimately, the Si-H_x passivation layer gave less frequency dispersion at flat band and a lower D_{it}, and the SiO_xN_y passivation layer yielded lower gate leakage and D_{it} when compared to the respective wet clean only devices.

4:40pm **SS+AS+EM-WeA8 Formation of Atomically Ordered and Chemically Selective Si-O-Ti Monolayer on $Si_{0.5}Ge_{0.5}$(110) for a MIS Structure via H_2O_2(g) Functionalization**, ***SangWook Park***, *J.Y. Choi,* University of California, San Diego*; E. Chagarov,* Univeristy of California, San Diego*; B. Sahu, S. Siddiqui,* GLOBALFOUNDRIES*; N. Yoshida, J. Kachian,* Applied Materials*; A.C. Kummel,* University of California, San Diego

To overcome challenges when scaling down silicon-based complementary metal-oxide semiconductor (CMOS) devices, SiGe has received much attention due to its high carrier mobility and applications in strain engineering. Extremely thin oxides with appropriate band offsets can be utilized to form unpinned contacts on SiGe for a metal-insulator-semiconductor (MIS) structure. The TiO_2 interfacial layer on Ge is known to form a MIS structure which reduces the tunneling resistance due to the nearly zero conduction band offset (CBO) between TiO_2 and Ge. In this study, formation of TiO_x monolayer on SiGe(110) via H_2O_2(g) functionalization was investigated using *in-situ* scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and x-ray photoelectron spectroscopy (XPS). H_2O_2(g) was employed instead of the conventional H_2O(g) oxidant since H_2O_2(g) can form a uniform monolayer of –OH ligands on the surface without subsurface oxidation which should be ideal for forming the most stable possible interface which is a layer of Si-O-Ti bonds. STM verified that clean $Si_{0.5}Ge_{0.5}$(110) surfaces were terminated with both Si and Ge adatoms. STS measurements indicated that the Fermi level of clean $Si_{0.5}Ge_{0.5}$(110) surfaces was pinned near midgap between the valence and conduction band edges due to the half-filled dangling bonds of the adatoms. In order to passivate the dangling bonds, atomic H was dosed onto clean $Si_{0.5}Ge_{0.5}$(110) at 300°C which unpinned the Fermi level as demonstrated by STS. XPS analysis showed a saturation dose of H_2O_2(g) at 25°C left the $Si_{0.5}Ge_{0.5}$(110) surfaces terminated with a monolayer of both Ge-OH and Si-OH sites. STS indicated that the Fermi level on H_2O_2(g) dosed $Si_{0.5}Ge_{0.5}$(110) was shifted to near the valence band edge due to the formation of surface dipoles induced by hydroxyl bonds. Tetrakis(dimethylamido)titanium (TDMAT) or titanium tetrachloride ($TiCl_4$) was subsequently dosed onto hydroxyl-terminated $Si_{0.5}Ge_{0.5}$(110) at 25°C forming Ti bonds on surface. Both TDMAT and $TiCl_4$ dosed $Si_{0.5}Ge_{0.5}$(110) surfaces were annealed at 300°C and XPS verified that the Ti-O bonds were totally transferred from Ge atoms to Si atoms forming exclusively Ti-O-Si bonds on $Si_{0.5}Ge_{0.5}$(110) surfaces consistent with the strong bonding between Si and oxygen pulling Si atoms toward the surface to bond with oxygen while pushing Ge atoms into the subsurface during the annealing. STM demonstrated an ordered TiO_x monolayer was formed with a row spacing which doubles the spacing of adatoms on clean $Si_{0.5}Ge_{0.5}$(110). In addition, STS indicated a TiO_x monolayer on SiGe(110) was unpinned and therefore can serve as an ultra-thin insulating layer for a MIS structure.

5:00pm **SS+AS+EM-WeA9 The Effect of Ultrasonic Treatment (UST) on the Defect Structure of the Si–SiO_2 System**, ***Daniel Kropman***, *T. Laas,* Tallinn University, Estonia

The effect of ultrasonic treatment (UST) on the defect structure of the Si–SiO_2 system by means of electron spin resonance(ESR),selective etching, MOS capacitance technique and secondary ions mass-spectroscopy is presented. The non-monotonous dependence of the defect densities on the US wave intensity has been observed. The influence of the UST frequency on the ESR signal intensity of the defect centres depended on the defects type and may be caused by vibration energy dissipation, which are a function of defect centres type. In the ESR spectra of Si samples a signal with g=1.9996 (Pa centres) connected with vacancy complexes is observed. After UST appears another signal with g=2.0055 (broken bonds of Si atoms). The influence of the US frequency and sample orientation on the ESR signal intensity varies for different centres. The frequency and orientation dependence of the ESR signal with g=l.9996 and the lack of this dependence for the centres with g=2.0055 show that vibration energy dissipation depends on the type of defect centers.Defect density at the interface grows with an increase of US wave intencity or changes nonmonotonously depending on the oxide thickness and crystallographic orientation. In the samples with thick oxide/0,6 mkm there is a maximum in the dependence of the charge carriers lifetime on the US wave amplitude and in the samples with thin oxides /0,3 mkm/ there is a minimum. This shows that the structural defects form electrically active centres and their density can be varied by US. The density of point defects and absorbed impurities at the Si–SiO_2 interface can be reduced and its electrical parameters improved by an appropriate choice of the UST and oxidation condition. US is widely used not only for materials treatment but in medicine as well (cancer treatment).

References:

[1]D.Kropman,V.Poll,L.Tambek,T.Karner,U.Abru.Ultrasonics 36(1998)10211025

[2]D.Kropman,S.Dolgov.Physica satatus Solidi (c) v.9,issue 10-11,pp.2173-2176,2012.

5:20pm **SS+AS+EM-WeA10 Adsorption of C_{60} Buckminster Fullerenes on a Carbon-free Hydrazine-modified Silicon Surface**, ***Fei Gao***[*]*, A.V. Teplyakov,* University of Delaware

Buckminster fullerene C_{60} was used as a model to understand the attachment chemistry of large molecules on amine-terminated semiconductor surfaces. The resulting interface may serve as a foundation for devices in such fields as solar energy conversion, biosensing, catalysis, and molecular electronics. In this work, a monolayer of buckminster fullerenes C_{60} was covalently attached to silicon surfaces using an efficient wet chemistry method. The starting chlorine-terminated Si(111) surface was initially modified with hydrazine to produce NH-NH functionality. Then the C_{60} fullerenes were reacted directly with this surface. The chemical state and surface topography of the C_{60}-modified surface were characterized by surface analytical spectroscopic and microscopic methods, including X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and atomic-force microscopy (AFM). The experimental results were also supported by computational investigation, density functional theory (DFT) calculations, that were performed to predict core-level energies of surface species formed and to propose the possible mechanism of surface reactions.

---

[*] **Morton S. Traum Award Finalist**

5:40pm **SS+AS+EM-WeA11 Passivation of SiGe Surfaces with Aqueous Ammonium Sulfide***, **Stacy Heslop**, A.J. Muscat,* University of Arizona

Ge and SiGe are promising materials for future p-type metal-oxide semiconductor field effect transistors (MOSFETs) due to their higher hole mobilities and narrower bandgap compared to Si. In contrast to silicon, Ge and SiGe readily oxidize in ambient air forming nonstoichiometric Ge oxides that are detrimental to the electrical performance of the device. One approach is to remove these oxides and passivate the surface. SiGe with molar ratios of 25 and 75% Ge were treated with aqueous ammonium sulfide, $(NH_4)_2S$, to deposit sulfur. The composition of the surface was measured using x-ray photoelectron spectroscopy (XPS) as a function of concentration and pH. The $(NH_4)_2S$ concentration was varied from 3 mM to 3 M, and the pH was varied from 10 to 8 using HCl and HF. Film thicknesses were measured with spectroscopic ellipsometry.

A fresh SiGe starting surface was produced by immersing in SC-1 (1:1:500 v/v) to form oxides and stripping the oxides using HF:HCl:H_2O (1:3:300 v/v). In the case of SiGe 25%, sulfides were not detected based on the S 2p XPS state for surfaces treated with $(NH_4)_2S$ (Figure 1a). The oxygen coverage increased with increasing $(NH_4)_2S$ concentration, forming primarily SiO_2 and a small coverage of GeO. The surface was enriched in Si and oxidized, and there was not enough Ge atoms exposed for S to bond to. HCl and HF were added to remove the Si and Ge oxides that formed. The addition of HCl and HF resulted in the deposition of sulfides on SiGe 25% (Figure 1b). The Si/Ge peak area ratio after oxide removal was 1.7. After immersion in 30 mM $(NH_4)_2S$ at a pH of 10 the surface composition was unchanged (Si/Ge=1.7). For the same $(NH_4)_2S$ concentration at a pH of 8 the surface was only slightly enriched with Si (Si/Ge=2.4). Overall, $(NH_4)_2S$ is not an effective passivation reagent for Si-rich SiGe surfaces due to the lack of S deposited and the undesirable oxides which form during processing. By dropping the pH to 8, less than a monolayer of S is deposited but oxides still remain. In contrast, SiGe 75% did not oxidize as a function of the $(NH_4)_2S$ concentration. Sulfur was detected based on the S 2p XPS state and the S coverage was independent of $(NH_4)_2S$ concentration. The sulfur thickness increased from about 2.3 Å for $(NH_4)_2S$ (30 mM or 1:100 v/v) at a pH of 10 to 3.4 Å for the same $(NH_4)_2S$ dilution at a pH of 8 (Figure 1c and d). These film thicknesses were approximated from XPS peak areas based on a single layer model for S on Ge. The deposition of the S layer did not affect the surface stoichiometry between oxide removal steps (Si/Ge=0.19) and 30 mM passivation (Si/Ge=0.20).

6:00pm **SS+AS+EM-WeA12 Novel Electrical Circuit Model for the Design of InGaAs/GaAs (001) Strained-Layer-Super-Lattice***, **Tedi Kujofsa**, J.E. Ayers,* University of Connecticut

Understanding lattice relaxation and dislocation dynamics has important implications in the design of highly functional and reliable semiconductor device heterostructures. Strain-layer-superlattices (SLSs) have been commonly used as dislocation filters whereby threading dislocations (TDs) can be removed by the insertion of a series of mismatched interfaces. The reduction of the threading dislocation in SLSs can be explained by the bending over of TDs associated with misfit segments of one sense by misfit dislocations having the opposite sense. Furthermore, the use of multilayered metamorphic buffer layers (MBLs) with intentionally mismatched interfaces may be used to take advantage of the strain compensation mechanism.

Previously, we developed a generalized energy minimization model, which determines the equilibrium configuration of an arbitrary compositionally-graded or multilayered heterostructure. The present work focuses on the development of a *novel electrical circuit* model for understanding equilibrium lattice relaxation in InGaAs/GaAs (001) strained-layer-superlattice heterostructures. This work focuses on the design of the SLS buffer layer of $In_xGa_{1-x}As$ deposited on a GaAs (001) substrate. The SL contains a set of 10 uniform layers with alternating mismatch. In other words, the SSL contains alternating uniform layers of $In_xGa_{1-x}As$ with indium compositions x and x + Δx respectively. For each structure, we present minimum energy calculations and show that for a given SLS total layer thickness h_{SLS}, it is possible to find the combination x and Δx such that it provides tight control of the in-plane strain of the strained-layer-superlattice. In addition, for each structure type we present minimum energy calculations by studying the (i) depth profile of strain and (ii) the misfit dislocation density profile. Most importantly, the use of the electrical circuit model allows the analysis of semiconductor heterostructures using a standard SPICE circuit simulator and provides an intuitive understanding of the relaxation process in these multilayered heterostructures.

Tribology Focus Topic
Room 101A - Session TR+AS+NS+SS-WeA

Nanoscale Wear: Applications to Nanometrology and Manufacturing

Moderators: Tevis Jacobs, University of Pittsburgh, Filippo Mangolini, University of Leeds, UK

2:20pm **TR+AS+NS+SS-WeA1 A Multi-Bond Model of Single-Asperity Wear at the Nano-Scale***, Y. Shao,* Johns Hopkins University*; T.D.B. Jacobs,* University of Pittsburgh*; **Michael L. Falk**,* Johns Hopkins University **INVITED**

Single-asperity wear experiments and simulations have identified different regimes of wear including Eyring- and Archard- like behaviors. A multi-bond dynamics model based on Filippov *et al.* [Phys. Rev. Lett. **92**, 135503 (2004)] captures both qualitatively distinct regimes of single-asperity wear under a unifying theoretical framework. In this model, the interfacial bond formation, wear-less rupture and transfer of atoms are governed by three competing thermally activated processes. The Eyring regime holds under the conditions of low load and low adhesive forces; few bonds form between the asperity and the surface and wear is a rare and rate-dependent event. As the normal stress increases the Eyring-like behavior of wear rate tends to break down. A nearly rate-independent regime holds under high load or high adhesive forces; bonds form readily and the resulting wear is limited by the sliding distance. In a restricted regime of normal load and sliding velocity, the dependence of wear rate on normal load is nearly linear and independent of sliding velocity, as described by the Archard equation. Detailed comparisons to experimental and molecular dynamics simulation investigations have illustrated both Eyring and Archard regimes and an intermediate cross-over between the two.

3:00pm **TR+AS+NS+SS-WeA3 Surface Chemical and Tribological Studies of Solid Lubricants for Space***, **Jeffrey Lince**,* The Aerospace Corporation **INVITED**

Successful operation of satellites and launch vehicles requires using multiple moving mechanical assemblies (MMAs). The correct choice of lubricants and tribocoatings is critical for the operation of spacecraft MMAs. However, the space environment is challenging. Examples include vibration during launch, thermal cycling on orbit, and the need to work effectively for missions up to twenty years in duration without lubricant replenishment. Especially challenging is the need for tribomaterials to withstand the vacuum of space during lengthy missions. As such, they must exhibit low vapor pressures, since evaporation of lubricants can result in loss from and premature failure of devices, as well as contamination of sensitive spacecraft components. Although unique synthetic liquid lubricants are used heavily in spacecraft for a variety of applications, solid lubricants are used with many devices because of their low vapor pressure, lack of migration, relative insensitivity to temperature changes, and low contamination potential. Soft solid lubricants such as molybdenum disulfide (MoS_2) and polytetrafluoroethylene (PTFE) have been used traditionally. More recently, hard low friction coatings such as hydrogenated diamond-like carbon have shown promise for operation in vacuum with existing spacecraft lubricants, or even unlubricated operation in vacuum. In addition, increasing interest in low friction nanoparticles has highlighted their potential utility. Tribomaterials show performance in vacuum that differs from that in air. This issue is important for spacecraft hardware, because it is often prohibitive to test them in a space-like environment, including vacuum, before launch. In addition, degradation during long-term storage can occur, and real-time storage studies correlating surface chemical changes with tribological performance are lacking. In this talk, results will be presented from studies done at The Aerospace Corporation that elucidate the effects of vacuum and temperature extremes on the tribological performance of important spacecraft tribomaterials. Emphasis will be on correlating surface chemical and tribological properties.

4:20pm **TR+AS+NS+SS-WeA7 Molecular Control of Friction***, **Roland Bennewitz**,* INM - Leibniz Institute for New Materials, Germany*; J. Blass, BL. Bozna,* INM - Leibniz Institute for New Materials*; M. Albrecht, G. Wenz,* Saarland University **INVITED**

Molecular films on surfaces can be used to control friction if it is dominated by adhesive shear rather than surface deformation. The underlying molecular mechanisms can be explored by high-resolution friction force microscopy.

We have developed a molecular toolkit for the control of friction and adhesion by supramolecular interactions in aqueous environments. The contacting surfaces are functionalized by cyclodextrin molecules. The interaction is mediated by ditopic connector molecules with hydrophobic end groups which form inclusion complexes with the cyclodextrin molecules on opposing surfaces. Significant friction and adhesion has been measured in atomic force microscopy experiments for connector molecules with adamantane, ferrocene, and azobenzene end groups.

For adamantane connector molecules, adhesion is found to be strongly dependent on the pulling rate due to a transition from subsequent peeling of individual bonds for slow pulling to multivalency effects at fast pulling. In contrast, friction does not depend on the sliding velocity [1].

The use of azobenzene connector molecules allows for switching of adhesion and friction by light stimuli [2]. Switching of friction by electrochemical stimuli for ferrocene connector molecules is less effective due to molecular interactions which are specific to the connector molecules but do not change with the potential [3]. We will discuss differences in rupture and rebinding dynamics for the three connector molecules and their influence on the rate dependence of adhesion and friction.

Cyclodextrin molecules have also been included in stiff polymers whose end groups are attached to tips or surfaces. The polymer-functionalized surfaces exhibit interesting variations of shearing and peeling mechanisms.

1. Blass, J., et al., Dynamic effects in friction and adhesion through cooperative rupture and formation of supramolecular bonds. Nanoscale, 2015. 7(17): p. 7674-7681.

2. Blass, J., et al., Switching adhesion and friction by light using photosensitive guest-host interactions. Chemical Communications, 2015. 51(10): p. 1830-1833.

3. Bozna, B.L., et al., Friction Mediated by Redox-Active Supramolecular Connector Molecules. Langmuir, 2015. 31(39): p. 10708-10716.

5:00pm **TR+AS+NS+SS-WeA9 Plasticity Controlled Friction and Wear in Single-Asperity Contacts***, **Izabela Szlufarska**, L. Zhao, A. Li, C. Tangpatjaroen, D. Grierson,* University of Wisconsin - Madison **INVITED**

One of the critical challenges in designing materials with superior tribological properties is the current lack of understanding of the microstructural evolution that takes place in sliding contacts. Phenomena that contribute to such evolution are grain growth and refinement, evolution of dislocation networks, and interaction of dislocations with interfaces. In this talk I will discuss examples of how we use multi-scale simulations and atomic force microscopy (AFM) experiments to determine the role of microstructural evolution and plastic deformation in friction and wear. Specifically I will discuss: (i) Our developments of a continuum model that couples grain growth, plastic deformation, and mechanics. This model combines for the first time the phase field method, crystal plasticity, and finite element analysis of mechanical contacts, and parameters for this model are determined from atomistic simulations and experiments. The new model is capable of simulating deformation at strain rates comparable to those encountered in AFM experiments. (ii) Results from our molecular-level simulations on the effects of dopants on strength and wear resistance of nanostructured metal alloys. (iii) Discovery from our complementary AFM and nanoindentation experiments that, although a harder material (silicon carbide) is typically more wear resistant than a softer material (silicon), this trend can be reversed with smaller contact sizes. The contact pressure is the same in both sets of experiments, and both are carried out in the regime where a plastic zone is well-developed. We demonstrate that this surprising finding is due to a transition from abrasive to adhesive wear, which for the first time is observed in single-asperity contacts. Our results show that surface chemistry can have a significant effect on sub-surface plastic deformation.

5:40pm **TR+AS+NS+SS-WeA11 Applying Analytical Roughness Models to Real Surfaces: Reconstructing the Power Spectral Density from Surface Topography Measurements***, **Tevis Jacobs**, A. Gujrati, S.R. Khanal,* University of Pittsburgh*; T. Junge, L. Pastewka,* Karlsruhe Institute of Technology (KIT), Germany

Surface topography is a critical factor for optical, mechanical, and tribological properties of materials. Many studies report single scalar roughness parameters that contain information over just a limited range of wavelengths. Analytical models of roughness have shown in recent years that properties such as stiffness, adhesion, and friction depend on the nature of roughness across many length scales. The power spectral density (PSD) is the mathematical instrument that provides a description of surface roughness as a function of scale. A truly quantitative analysis of surface roughness in terms of the PSD is necessary to validate and apply these analytical roughness models. However, this is currently limited by: (A) inconsistencies in the way that the quantitative PSD is computed; (B) bandwidth-limits of conventional surface metrology; and (C) instrumental artifacts at the smallest scales. Here, we demonstrate these limitations – first, by comparing the various forms of the PSD, then by computing the PSDs both for simulated and experimental surfaces.

We show that experimentally-determined PSDs suffer three types of systematic error, each of which will hinder quantitative comparison to models. We demonstrate strategies for detection and mitigation of these artifacts, to ensure accurate and reliable PSDs. A novel web-based application has been created and made available for general use which computes accurate PSDs and assesses the limits of their reliability. This enables the application of analytical roughness models to calculate upper and lower bounds of surface properties.

Finally, we report on the roughness characterization of an ultrananocrystalline diamond (UNCD) surface over the range from Angstroms to centimeters. This range of characterization enables quantitative comparison with rough-surface adhesion models. By elucidating experimental barriers to accurate surface characterization, and by demonstrating solutions to these barriers, this work facilitates the application of analytical roughness models to real-world surfaces – both to predict and tailor surface properties.

6:00pm **TR+AS+NS+SS-WeA12 Universal Ageing Mechanism for Static and Sliding Friction of Metallic Nanoparticles***, M. Feldmann, **Dirk Dietzel**, A. Schirmeisen,* Institute of Applied Physics, Justus-Liebig-University Giessen, Germany

On the macroscale, the distinct difference between static and sliding friction can well be explained by the phenomenon of contact ageing, which is typically related to an increase of contact area with time within a multi asperity interface model. On the nanoscale, however, the role of contact ageing is less clear, especially when considering nanoscale asperities of constant size.

Recently, the role of contact ageing for nanoscale friction dynamics was analyzed for antimony nanoparticles sliding on HOPG. The antimony nanoparticles have been prepared by thermal evaporation on HOPG and comprise an ideal model system with atomically flat interfaces of constant size where friction can be described by the concept of structural superlubricity [1]. Friction of the particles was assessed by nanomanipulation techniques and it was found, that sliding friction can be described as a complex process of thermally activated contact ageing and bond breaking [2]. Further measurements have now revealed, that the particle movement follows an irregular stick slip pattern, where the slip events can be considered as recurring contact renewal, while the stick times can be interpreted as the age of the contact. By correlating the stick times with the lateral force values measured for contact breaking, we found that our system can well be described by logarithmic ageing [3], as it might be expected by assuming atom by atom relaxation processes at the interface.

To check whether ageing during sliding motion is fundamentally different from ageing under stationary conditions, we have performed additional “slide hold slide” measurements [4] and found that in both cases ageing can be described by exactly the same logarithmic function. This indicates, that the strength of the contact is determined by the ageing time but independent of the kinetic conditions. This means that static and sliding friction can be described by a universal ageing law where the age of the contact is the crucial parameter.

[1] D. Dietzel, M. Feldmann, H. Fuchs, U.D. Schwarz, A. Schirmeisen, Phys. Rev. Lett. 111, 235502 (2013)

[2] M. Feldmann, D. Dietzel, H. Fuchs, A. Schirmeisen, Phys. Rev. Lett. 112, 155503 (2014)

[3] M. Feldmann, D. Dietzel, A. Tekiel, J. Topple, P. Gruetter, A. Schirmeisen, Phys. Rev. Lett. 117, 025502 (2016)

[4] Q. Li, T.E. Tullis, D. Goldsby, R. W. Carpick, Nature 480, 233-236 (2011)

Applied Surface Science
Room 101B - Session AS+SS-ThM

Depth Profiling, Buried Interfaces, and 3D Analyses

Moderators: Gregory Fisher, Physical Electronics USA, Karen Gaskell, University of Maryland, College Park

8:00am **AS+SS-ThM1 Pushing the Limits of Bonded Multi-Wafer Stack Heights while Maintaining High Precision Alignment**, ***Alireza Narimannezhad***, *J. Jennings, M.H. Weber, K.G. Lynn,* Washington State University

The last decade in advanced microelectronics has shown great interest in three-dimensional architectures, which was paved by multi-wafer alignment technologies. However, many limitations remain in the fabrication of ultratall stacks as the alignment becomes more challenging and very costly. In this paper, a new cost-effective alignment technique was employed using a set of sapphire rods in through-wafer holes. Cross-sectional analysis, edge profilometry, and electron transmission tests showed ~2 µm alignment tolerances over 1 cm and ~4 µm over 10 cm tall stacks. An off-angle gold sputtering method was developed to fully coat vias of 5:1 aspect before bonding. Also, a new *Stamping* technique is introduced to coat the vias to a desired height where necessary. In this study, parallel microtubes with aspect ratios of 1,000:1 were formed by aligning ~200 wafers, each including 20,000 gold-coated vias for storing charged particles.

8:20am **AS+SS-ThM2 Porous Si Stack Analysis by Model Based Infrared Reflectometry (MBIR)**, ***Sukti Chatterjee***, *L. Scudder, P. Narwankar,* Applied Materials Inc.

In 1956, Porous silicon (PS) was accidentally discovered by Uhlir at Bell Laboratories [1], and t he material was very much ignored. Later (70's and 80's) porous Si was found to be useful because its high surface area [2-5] for various applications, like microcavity, broadband AR coating, mid infrared LEDs, chemical Sensors, smart Dust, pressure Sensor, photonic crystal. Recent interest of porous Si is in the biomedical *field [6] with wide range of applications*, ex. drug delivery, cancer therapy, and tissue engineering. For diverse applications, single or multilayers porous Si stacks are required. In this abstract we present our metrology invention for single or multilayers porous Si stacks analysis.

We introduce a novel approach to characterize the different Si film stacks by using Model Based Infrared Reflectometry (MBIR). We believe, we are first group to apply the technique for analyzing various multilayer Si stacks. The film stack thickness has varied between 1 µm to more than 100 µm. Thick layers of silicon are opaque in the UV-VIS wavelength range, and IR wavelengths are ideal for measurements of such films. The ability to specify a film stack in the MBIR analysis model makes the technique more versatile, compared to traditional FTIR. We will present in the conference how the IR optical properties of PS can be described by Bruggeman Effective Medium Approximation (EMA), employing a standard multilayer reflectance model. To validate the MBIR results x-SEM and Gravimetric analysis have been used. The results have shown MBIR to be a suitable technique for characterization and production monitoring of the process steps associated with the new porous silicon applications field.

References

1. Uhlir, A., Electrolytic shaping of germanium and silicon. Bell System Tech. J., 1956. 35: p. 333-347.

2. Gupta, P., V.L. Colvin, and S.M. George, Hydrogen desorption kinetics from monohydride and dihydride species on Si surfaces. Phys. Rev. B, 1988. 37(14): p. 8234-8243.

3. Gupta, P., et al., FTIR Studies of H2O and D2O Decomposition on Porous Silicon. Surf. Sci., 1991. 245: p. 360-372.

4. Dillon, A.C., et al., FTIR studies of water and ammonia decomposition on silicon surfaces. J. Electron Spectrosc. Relat. Phenom., 1990. 54/55: p. 1085-1095.

5. Dillon, A.C., et al., Diethylsilane Decomposition on Silicon Surfaces Studied using Transmission FTIR Spectroscopy. J. Electrochem. Soc., 1992. 139(2): p. 537-543.

6. Porous Silicon for Biomedical Applications, Edited by: H.A. Santos ISBN: 978-0-85709-711-8

8:40am **AS+SS-ThM3 Applications of Atom Probe Tomography on 3D Semiconductor Devices**, ***AjayKumar Kambham***, *D. Flatoff, P.A.W. van der Heide,* GLOBALFOUNDRIES U.S. Inc. **INVITED**

One of the aims in CMOS device development is to reduce power consumption while increasing performance. Pivotal to this, is the critical need to engineer dopant profiles, and to define the formation of the appropriate junctions. Tied to this is the increased severity of short channel effects (SCEs) as dimensions are decreased, hence the reason to move to 3D structures in the form of FinFETs. One type of SCE that is known to cause performance degradation is Drain Induced Barrier Lowering (DIBL). To reduce DIBL, dopant junction profiles are made more abrupt. This can be done through the introduction of Sigma/cavity, fully depleted silicon-on-insulator (FDSOI) structures and the modulation of stress through optimal engineered epitaxial buffer layers. To assess the quality of interfaces in these different structures over nanometer scale regions requires the use of analysis techniques such as Atom Probe Tomography (APT) and Transmission Electron Microscopy (TEM). This presentation will discuss the ability of APT to extract the critical information of interest to device engineering.

9:20am **AS+SS-ThM5 Analysis of ALD/CVD Thin Film Conformality using Lateral High Aspect Ratio (LHAR) Structures: Experimental Characteristics and Proposed Classifications**, ***Riikka Puurunen***, VTT Technical Research Centre of Finland*; J. Dendooven, V. Cremers, C. Detavernier,* Ghent University, Belgium

High conformality—the ability of a thin film to cover a complex three-dimensional substrate uniformly—is a key advantage of atomic layer deposition (ALD) compared to chemical vapor deposition (CVD) and physical vapor deposition (PVD) processes. More than 700 ALD processes (with unique reactant pairs/activation) have been reported, as calculated from Ref. [1]. Conformality has been experimentally studied for a small minority of these, most likely because of the lack of easily available test structures and accessible methods of analysis.

When conformality is investigated, most typically, vertical trenches (or holes) etched into silicon, typically with aspect ratio (AR) up to around 50:1, are used and the results are analysed point by point by cross-sectional electron microscopy. Comparison of results obtained in different studies is difficult because of the lack of standard test structures and standard means of analysis, and the large variety of process conditions that are used. The theoretical framework for interpreting the conformality results is also underdeveloped.

To develop the conformality analysis, we have reported on macroscopic [2, 3] and microscopic [4] lateral high aspect ratio (LHAR) test structures. In contrast to vertical HAR, LHAR structures allow one to investigate thin film thickness and properties in very demanding aspect ratios (>10 000:1) and obtain accurate information of film thickness and properties along the feature by standard means of measurement such as ellipsometry and reflectometry. The purpose of the present work is to compare results obtained for different thin film processes in different test structures (our own + literature) using the highly studied [1, 5] Me3Al/H2O ALD process as baseline. We propose a classification scheme for how the thickness line profiles are expected to vary inside LHAR structures in different cases of characteristic governing growth chemistries.

Acknowledgements: This work has been funded by the Finnish Centre of Excellence in Atomic Layer Deposition, BOF-UGent, FWO-Vlaanderen and SIM-Flanders (TRAP-FUNC project). Feng Gao and Meeri Partanen are thanked for fabricating the microscopic LHAR structures.

References:

[1] V. Miikkulainen et al., J. Appl. Phys. 113 (2013) 021301.

[2] J. Dendooven et al., J. Electrochem. Soc. 156 (2009) P63.

[3] J. Dendooven et al., J. Electrochem. Soc. 157 (2010), G111.

[4] F. Gao et al., J. Vac. Sci. Technol. A, 33 (2015), 010601.

[5] R. L. Puurunen, J. Appl. Phys. 97 (2005) 121301.

9:40am **AS+SS-ThM6 *In Situ* Liquid SIMS Investigation of Chemical Components of the Solid-Electrolyte Interface in Li Ion Batteries**, ***Zihua Zhu***, *C. Wang, Y. Zhou, D.R. Baer, W. Xu, R. Cao, X. Yu, P. Yan, R. Zhao,* Pacific Northwest National Laboratory

Since the birth of Li-ion battery, Solid-Electrolyte Interface (SEI) has been a hot research topic, and numerous efforts have led to some information about its chemical composition, formation mechanism and degradation process. However, critical questions that can enable the design of advance battery systems remain unanswered because it has been very difficult to molecularly examine the SEI layer during battery operation. For example, in situ TEM has been used to study the formation process of the SEI layer in Li ion batteries; however, mostly morphological information, but very limited chemical information is obtained. In situ liquid SIMS was developed in Pacific Northwest National Laboratory (PNNL) in the last several years, and it has proven a very promising new technique to provide both elemental and molecular information at solid-liquid interfaces. In this work, a model Li-ion battery was designed for in situ liquid SIMS analysis of SEI layer. A ~70 nm thick Cu film was deposited onto a SiN membrane, which served as anode. Cathode was traditional $LiCoO_2$. 1.0M $LiPF_6$ in EC (ethylene carbonate)/DMC (dimethyl carbonate) was used as electrolyte. Li_2O and LiOH are found in the SEI layer, while very little LiF is observed, indicating LiF is not an important component in the SEI layer. More interestingly, solvent molecules are found in the SEI layer, and the major component is DMC but not EC. In addition, very little PF_6^- is found in SEI layer. This is the first time that molecular information of the SEI layer is obtained, and the new information will greatly advance understanding formation mechanism and degradation process of SEI layer.

11:00am **AS+SS-ThM10 Electronic and Physical Changes to Soft Materials Caused by Gas Cluster Sputtering**, ***Christopher Goodwin***, *Z.E. Voras, T.P. Beebe, Jr.,* University of Delaware

The development and application of gas cluster ion sputtering (GCIS) of soft materials opens the ability to perform 3D analysis without removing the sample from a vacuum environment. GCIS has been used to remove material from the surface of some samples without leaving behind a significant amount of damaged material. This allows for depth profiling and sample cleaning in vacuum, without loss of chemical information. The soft sputtering standard Irganox 1010 has been used to study topological effects of GCIS with atomic force microscopy (AFM) while chemical changes were monitored with X-ray Photoelectron Spectroscopy (XPS). In addition to Irganox 1010, polyaniline has been studied due to its importance as an organic conductive material, allowing for many applications such as a solar cells, antistatic and corrosion-resistant coatings, and superconductors. GCIS was used to depth profile into thin films of polyaniline, resulting in some topological (AFM) and chemical changes (XPS). Our interest is in exploring how these changes caused by GCIS sputtering affect the electronic band structure of conductive polymers.

11:20am **AS+SS-ThM11 FIB-TOF Characterization of Organic and Organic/Inorganic Structures**, ***David Carr***, *G.L. Fisher, S.R. Bryan,* Physical Electronics; *S. Iida, T. Miyayama,* ULVAC-PHI, Japan

1. Introduction

Probing the sample chemistry beyond the surface region with ion beam sputtering is subject to practical limitations which include preferential sputtering, accumulated sputter beam damage, inclusions, and voids. These effects can result in a distortion or complete loss of the true chemical distribution as a function of depth.

In situ FIB milling and sectioning with TOF-SIMS chemical imaging (3D FIB-TOF tomography [1]) is an alternative approach to achieve 3D chemical imaging of complex matrix chemistries. The FIB milling can minimize or eliminate artifacts caused by sputter depth profiling from the surface.

For matrices with organics components, however, FIB beam-induced chemical or molecular damage may limit the detection of characteristic molecular signals. The characteristic molecular signals can often be recovered with cluster ion polishing to remove the organic FIB damage.

2. Method

The 3D chemical characterization of organic and organic/inorganic mixed composition structures was achieved utilizing FIB-TOF on a PHI TRIFT *nanoTOF* II (Physical Electronics, USA) imaging mass spectrometer equipped with the new parallel imaging MS/MS [2,3]. The spectrometer's large angular acceptance and depth-of-field maintain high mass resolution and high mass scale linearity in this challenging geometry.

3. Results

Results will be presented for structures with mixed organic phases and mixed organic/inorganic phases. The FIB-TOF results will be compared with corresponding sputter depth profiling results to highlight the relative advantages of the two techniques along with potential complicating factors to the analyses. The high sensitivity of the TOF-SIMS technique is not limited to strong organic matrix peaks. Data will be presented showing the ability to probe the 3D distribution of polymer additives in a sample. The identity of the additives is confirmed using the newly developed parallel imaging MS/MS option for the *nanoTOF* II. The ability to study buried organic structures with FIB-TOF and then conclusively identify the detected species using MS/MS is a powerful new development for the field of TOF-SIMS.

4. References

[1] A. Wucher, G.L. Fisher and C.M. Mahoney, Three-Dimensional Imaging with Cluster Ion Beams (p. 207-246) in *Cluster Secondary Ion Mass Spectrometry: Principles and Applications*, C.M. Mahoney (Ed.), Wiley & Sons, N.J. (2013).

[2] P.E. Larson, J.S. Hammond, R.M.A. Heeren, G.L. Fisher, *Method and Apparatus to Provide Parallel Acquisition of MS/MS Data*, U.S. Patent 20150090874, 2015.

[3] G.L. Fisher, J.S. Hammond, P.E. Larson, S.R. Bryan, R.M.A. Heeren, *SIMS XX Proceedings*, D. Castner (Ed.), Wiley, N.J. (2016) DOI: 10.1116/1.4943568.

11:40am **AS+SS-ThM12 Molecular Depth Profiling with a New Hybrid 3D SIMS instrument for Improved Molecular Identification**, ***Alexander Pirkl***, *R. Moellers, H.F. Arlinghaus,* ION-TOF GmbH, Germany; *N.J. Havercroft,* ION-TOF USA; *E. Niehuis,* ION-TOF GmbH, Germany; *A.A. Makarov, S. Horning,* Thermo Fisher Scientific; *R. Havelund, M.K. Passarelli, A.G. Shard, I.S. Gilmore,* National Physical Laboratory, UK

Introduction

Depth profiling of organic layers for optical and electronic devices can be ideally performed using gas cluster ion beams (GCIB) in combination with time-of-flight secondary ion mass spectrometry (TOF-SIMS). For optimum performance a dual beam approach is utilized, employing a lower energetic quasi DC sputter beam for material removal and a short pulsed small spot analysis beam for optimal mass spectral and imaging performance.

However molecular identification of unknown substances, e.g. contaminants, is usually hampered by constraints in mass resolution and mass accuracy of the TOF analyser. Furthermore ions generated in the sputter phase of the dual beam experiment are lost for the MS analysis. In order to overcome these limitations a TOF/Orbitrap^{TM}-SIMS hybrid mass analyser instrument was developed.

Methods

A prototype SIMS instrument with a hybrid TOF/Orbitrap mass analyser was utilized for acquisition of organic depth profiles. During sputtering with 5-20 keV argon clusters secondary ions can be detected using the Q Exactive^{TM} HF mass analyser. Selective ion gating was implemented to avoid artefacts from the crater walls. *In situ* tandem MS analyses of the most abundant peaks were used to confirm the mass assignments. Imaging TOF analysis with high lateral resolution was performed on the same instrument using short pulses from a 30-60 keV Bi-liquid metal ion gun (LMIG) and a dedicated TOF.SIMS V analyser for comparative measurements.

Preliminary Data

Molecular depth profiles were acquired using GCIB induced desorption in a single beam approach from organic test structures and organic LED materials. The high mass resolution of 240 000 of the Q Exactive HF mass spectrometer proved to be essential for separation of otherwise overlapping ion signals. Molecular assignments based on the high mass accuracy below 3 ppm were validated using tandem MS analysis. Up to 5 decades of dynamic range and a depth resolution below 8 nm were found to be possible with this approach leading to unprecedented depth profiling results.

Depth profiles and according spectra are compared to the classical dual beam approach. While depth resolution is similar, differences in the relative signal intensities were observed in spectra from the two different ion beams. Implications for the analysis of biological samples will be discussed.

12:00pm **AS+SS-ThM13 3-D Analysis of Binding-Medium Degradation as Related to Renaissance-Era Artwork**, ***Zachary Voras***, *C.M. Goodwin,* University of Delaware; *J.L. Mass,* Rijksmuseum; *K.R. DeGhetaldi,* Winterthur Museum; *T.P. Beebe, Jr.,* University of Delaware

In historical art objects, binding-medium degradation involves complex chemistries that can occur at the surface or interface of a paint layer. These can propagate inward toward the bulk material, caused by inherent impurities within the paint that migrate throughout the paint layer. These effects can cause mechanical failure due to binding-medium degradation, primarily observed as paint-layer flaking, spalling, and fracture. Our prior research performed on Renaissance-era artwork has indicated two major correlations to the severity of binding-medium degradation: i) depletion of long-chain fatty acid components within the binding medium of a paint layer, and ii) alteration of the amino-acid composition of proteinaceous materials comprising the binding medium. In this study, the effects of controlled aging factors (i.e., heat, humidity, and UV exposure) on thin films of egg tempera were observed through the use of x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The newly available technology of gas cluster ionization sources (GCIS) allows for the ability to depth profile through some soft organic and biological materials with no little or no ion-induced damage. By using an argon-cluster ion beam to depth profile through a degraded thin film, a 3-dimensional analysis of short- and long-range degradation effects, followed by XPS and ToF-SIMS, respectively, was performed. Since ultramicrotomy is an established sample-preparation technique in the art conservation field, results of GCIS will be compared to ultramicrotomy as sample preparation method for organic and biological thin films.

Electronic Materials and Photonics
Room 102A - Session EM+AC+SS+TF-ThM

Radiation Detection Materials and Devices

Moderators: Sean King, Intel Corporation, Michelle Paquette, University of Missouri-Kansas City

8:00am **EM+AC+SS+TF-ThM1 Novel High Energy Resolution Scintillator Detectors**, ***Arnold Burger***, *E. Rowe, L. Matei, P. Bhattacharya, M. Groza,* Fisk University; *K. Stassun,* Vanderbilt University; *A. Stowe,* Consolidated Nuclear Security Y-12; *N. Cherepy, S. Payne,* Lawrence Livermore National Laboratory **INVITED**

This presentation will review the status of bright scintillators for gamma and thermal neutrons applications. The scintillators are based on single crystals of halides or selenides that are activated by rare earth ions or are self activated. The main features that make them attractive for biological, medical, space and national security applications are: (i) high stopping power of radiation, (ii) high energy resolution, (iii) fast decay time, (iv) crystal growability at low cost, (v) good gamma/neutron discrimination via pulse shape analysis, and (vi) good spectral matching with silicon photodetectors for compact and low power devices and instrumentation.

8:40am **EM+AC+SS+TF-ThM3 Improved p–n Heterojunction Device Performance Induced by Irradiation in Amorphous Boron Carbide Films**, ***George Peterson***, *Q. Su,* University of Nebraska - Lincoln; *Y. Wang,* Los Alamos National Laboratory; *P.A. Dowben, M. Nastasi,* University of Nebraska - Lincoln

Amorphous hydrogenated boron carbide films (a-$B_{10}C_{2+x}$:H_y) on Si p–n heterojunctions were fabricated utilizing plasma enhanced chemical vapor deposition (PECVD). These devices were found to be robust when irradiated with 200 keV He^+ ions. For low doses of irradiation, contrary to most other electrical devices, the electrical performance improved. On the heterojunction I(V) curve, reverse bias leakage current decreased by 3 orders of magnitude, series resistance across the device decreased by 64%, and saturation current due to generation of electron–hole pairs in the depletion region also decreased by an order of magnitude. It is believed that the improvements in the electrical properties of the devices are due to an initial passivation of defects in the a-$B_{10}C_{2+x}$:H_y film resulting from electronic energy deposition, breaking bonds and allowing them to reform in a lower energy state, or resolving distorted icosahedron anion states.

9:00am **EM+AC+SS+TF-ThM4 Amorphous Hydrogenated Boron Carbide for Direct-Conversion Solid-State Neutron Detection**, ***Gyanendra Bhattarai***, *T.D. Nguyen, S. Dhungana, A.N. Caruso, M.M. Paquette,* University of Missouri-Kansas City

The trade-off between conversion layer thickness and penetration depth of primary reaction products inherently limits the efficiency of conversion-layer solid-state neutron detectors, motivating the need for direct-conversion solutions. Direct-conversion devices, in principle, offer nearly unity detection efficiency, a minimum of fabrication steps, large-area scalability, and high efficiency density, all of which are essential for small-sized neutron spectrometers as well as for large-area detectors. However, to date, there is a lack of well-developed semiconductor materials with high thermal neutron absorption that also lead to energetic reaction products amenable to detection. Amorphous hydrogenated boron carbide (a-B_xC:H_y), a complex disordered semi-insulating material, is a promising candidate because of its high neutron absorption and high resistivity. Additionally, excellent mechanical, chemical, and thermal stability make it suitable for harsh detection environments. The main challenges, however, in the study of a-B_xC:H_y are its low charge carrier mobility, the difficulties associated with making proper electrical contacts for accurate charge transport measurements, and the inefficacy of traditional experimental techniques and interpretations to address the complex nature of the material (i.e., it is a high-resistivity, disordered, molecular solid). This contribution will present an overview of how a-B_xC:H_y may lead to high-efficiency neutron detectors based on theoretical simulations, the study of its charge transport metrics focusing mainly on charge carrier mobility and lifetime, and the development of proper electrical contacts on PECVD grown thin films of this material.

9:20am **EM+AC+SS+TF-ThM5 Radiation Damage of Low-κ Interlayer Dielectrics Studied with Electrically Detected Magnetic Resonance**, ***Michael Mutch***, *P.M. Lenahan,* Pennsylvania State University; *S.W. King,* Intel Corporation

Radiation effects of MOS devices have been extensively studied due to the demand for electronic devices in space applications.[1] The scaling of these MOS devices will lead to an eventual need for low-dielectric constant (i.e., low-κ) dielectrics to reduce parasitic capacitances associated with scaling of back-end-of-line interlayer dielectrics (ILDs). However, little is known about radiation effects of low-κ ILDs. We utilize electrically detected magnetic resonance (EDMR) via spin-dependent trap-assisted tunneling (SDTAT) to study point defects in porous low-κ a-SiOC:H systems before and after exposing samples to radiation damage. SDTAT/EDMR has the sensitivity and analytical power to specifically identify only those defects which are involved in electronic transport. Due to the inherent complexity of the a-SiOC:H systems, multiple frequency EDMR is utilized to better understand defect structure when featureless spectra are present.

The a-SiOC:H films are grown via PECVD, and exhibit carbon dangling bonds prior to porogen removal via UV-annealing.[2] After porogen removal via UV treatment, it has been shown, via multiple frequency EDMR, that silicon dangling bonds are the dominating defect center responsible for SDTAT in these films.[2] The porous a-SiOC:H systems were subjected to a 15 Mrad total dose via a cobalt-60 dry cell gamma-ray source while simultaneously applying either positive, negative, or no bias. We find that the post-radiation IV curves are a strong function of the biasing conditions which were applied during radiation. This likely indicates that electron and hole traps will both play a role in radiation damage effects in these systems. We find that the EDMR response amplitude is greatly increased (by a factor of 4 or greater) after irradiation for all biasing conditions. This result indicates a substantial increase in the density of defects involved in electronic transport. Multiple frequency EDMR measurements suggest that the generated defects are primarily silicon dangling bonds.

[1] J. R. Schwank et al., IEEE Trans. Nuc. Sci. **55**, 1833 (2008).

[2] M. J. Mutch et al., J. Appl. Phys. **119**, 094102 (2016).

9:40am **EM+AC+SS+TF-ThM6 Modeling Unit Displacement Damage in Amorphous Silicon Oxycarbides**, ***Hepeng Ding***, *M. Demkowicz,* MIT

Amorphous silicon oxycarbide (SiOC) is of great technological interest. To study its potential application as a radiation-resistant material, we present *ab initio* modeling investigations of unit displacement damage processes in it using density functional theory. We model 0.1 keV primary knock-on atoms (PKA) in SiO_2, SiOC, and hydrogenated SiOC (SiOCH) with different hydrogen levels. We find that PKAs affect the carbon-clustering tendency in both SiOC and SiOCH. Our results also suggest that SiOCH is irradiation indifferent, i.e., upon PKA, the potential energy does not increase and there is no major structural change.

This work was funded by the DOE Office of Nuclear Energy, Nuclear Energy Enabling Technologies, Reactor Materials program, under contract No. DE-NE0000533. Computational support was provided by DOE-NERSC and DOE-OLCF.

11:00am **EM+AC+SS+TF-ThM10 Position-Sensitive 3D CZT Gamma-Ray Detectors with Thickness Up to 50 mm**, ***Ralph James***, *A.E. Bolotnikov, G.S. Camarda, Y. Cui, G. De Geronimo, J. Fried, A. Hossain, G. Mahler, U. Roy, E. Vernon, G. Yang,* Brookhaven National Laboratory **INVITED**

High-granularity position-sensitive detectors allow for accurate charge-signal corrections to overcome non-uniformities in the devices' responses caused by crystal defects. The operational principle of position-sensitive detectors is analogous to the well-known drift ionization chambers used for tracking charged particles and detecting the interaction events generated by gamma rays. Advantages of the position-sensitive designs were realized in a number CZT detectors, including CAPture™, hemispherical, Frisch-ring, capacitive Frisch-grid and even pixel detectors in which pixel contacts act like shielding electrodes. In our virtual Frisch-grid (VFG) devices, the sensing strips are separated from the crystal surfaces by a thin insulating layer, as it was originally done in other Frisch-grid designs. The amplitudes of the signals readout from the strips are used to measure the coordinates of the interaction points and correct the response non-uniformities. The drift time and the cathode-to-anode ratio were used to independently evaluate the location of the interaction points in Z directions, correct for electron loss, and identify and reject the events for which the charge losses caused by defects are so great that they cannot be corrected accurately. Combining these two techniques allows us to significantly enhance the spectral responses of position-sensitive VFG detectors, and to significantly improve their performance. Such high-granularity position-sensitive detectors open up the opportunity for using thicker, less expensive crystals. We demonstrated that today's CZT material is suitable for detectors with up to 40-50-mm drift distances, provided that the detectors have the ability to correct their response non-uniformities on a scale comparable to the sizes of electron clouds, which is ~100 m m. We employed an ASIC and data-acquisition system developed by BNL's Instrumentation Division for arrays of VFG detectors. For each detector we used 6 ASIC channels to read the negative signals from the cathode and from four position-sensing pads, and the positive signals from the anode. For each interaction event, the anode signal correlates with the *X* and *Y* values converted from the 4 strip signals and Z coordinate evaluated from the cathode signal. This relationship allows us to correct each anode signal in accordance with the location of the interaction point. We selected the voxel sizes to achieve the best performance, typically ~30x30 pixels in *XY*-space and ~100 segments in the Z-direction. The performance of thick position-sensitive VFG detectors fabricated from CZT crystals will be reported for a variety of radioactive sources and testing conditions.

11:40am **EM+AC+SS+TF-ThM12 Understanding the Electrical Properties of U_3O_8 for Direct Conversion Neutron Detectors***, **Brandon Shaver**, S. Lawson, B. Musicó,* The University of Tennessee Knoxville*; S. Dhungana, G. Bhattarai, M.M. Paquette, A.N. Caruso,* University of Missouri-Kansas City*; T. Meek,* The University of Tennessee Knoxville

With a high neutron fission cross section for ^{238}U, U_3O_8 is one of a series of uranium oxide semiconductors that may be suitable for direct-conversion neutron detectors. However, the electrical transport properties of U_3O_8 are not well-characterized: the literature that does exist reports largely inconsistent resistivity values, and similarly contradictory values for work function. One of the reasons for these wide ranges is that slight changes in stoichiometry in urania-based systems, UO_2 for example, can have a tremendous influence on electrical properties; however, the details of these effects are not well-understood. We seek to rigorously characterize the electrical transport properties in U_3O_8 to understand the range of values that can be achieved and—importantly—their relationship to fabrication method as well as composition/microstructure. Samples of U_3O_8 pellets have been made by uniaxial pressing of U_3O_8 powder and subsequent sintering under various conditions. These samples have then been characterized to determined their microstructure, exact stoichiometric composition, and electrical properties. By carefully studying the relationship between sample preparation and electrical properties, we aim to establish the ability to control and optimize the electrical transport metrics of U_3O_8 critical for detection applications.

12:00pm **EM+AC+SS+TF-ThM13 Radiation Damage in 4H SiC nMOSFETs Detected by Electrically Detected Magnetic Resonance***, **Ryan Waskiewicz**, M.A. Anders, P.M. Lenahan,* Pennsylvania State University*; A.J. Lelis,* U.S. Army Research Laboratory

Metal oxide semiconductor field effect transistors (MOSFETs) based upon 4H-SiC have great promise in high power and high temperature applications. An area of substantial interest is in outer space, where the devices will be subjected to ionizing radiation. The effects of ionizing radiation have been well studied in Si-based MOS devices, where E' and Pb centers play dominating roles as oxide and interface traps respectively. Very little is known about the types of defects created in radiation damage in SiC MOSFETs. In order to develop a fundamental understanding of ionizing radiation effects, we have performed a study utilizing electrically detected magnetic resonance (EDMR) via the bipolar amplification effect (BAE) [1]. We observe several changes between the pre- and post-irradiation EDMR results, which strongly indicate change in the structure of the SiC/SiO_2 interface region but relatively little change in the number of observed interface defects.

The devices used in this study had 50 nm thick thermally grown gate oxides in N_2O. After oxidation, the devices were subjected to the standard post-oxidation NO anneal at 1175°C. The n-channel 4H-SiC MOSFETs have been subjected to 6MRads of gamma radiation from a 60Co gamma source while a 10V bias applied to the gates. Standard transistor characteristic measurements made on the devices before and after irradiation indicate a threshold voltage shift of approximately -4V. We observed several significant changes in the EDMR response, the most obvious EDMR differences are in the amplitude of the BAE EDMR measurements as a function of applied gate voltage. The maximum EDMR amplitude increased by a factor of 7 as a result of the irradiation, and the gate bias at which the peak occurred shifted by approximately -4V, consistent with the approximate -4V shift in threshold voltage. BAE measurements measure spin dependent recombination due to deep level defects at and very close to the SiC/SiO_2 interface. We find significant change in the EDMR line shapes, observing significant post-irradiation broadening of the spectra. Surprisingly, we are unable to observe either silicon or carbon dangling bond defects in these preliminary measurements. It is clear from the measurements that both the pre-irradiation and post-irradiation measurements are dominated by silicon vacancies on the SiC side of the interface. EDMR measurements as a function of microwave power show quite significant changes in the saturation behavior of the magnetic resonance. These results suggest significant structural changes in the interface region.

[1] Thomas Aichinger and Patrick M. Lenahan, Appl. Phys. Lett. **101**, (2012)

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 103A - Session HC+SS-ThM

Dynamics of Gas-surface Interactions in Heterogeneous Catalysis

Moderator: Daniel Killelea, Loyola University Chicago

8:00am **HC+SS-ThM1 Adsorption and Hydrogenation of Acrolein on Ru(001)***, **Dominic Esan**, Y.D. Ren,* University of Illinois at Chicago*; I.B. Waluyo,* Brookhaven National Laboratory*; M. Trenary,* University of Illinois at Chicago

The partial hydrogenation of α, β-unsaturated aldehyde s is an important step in several synthetic industrial processes especially in the fine chemicals and pharmaceutical industries. Generally, it has been established that the thermodynamics of the catalytic hydrogenation of these unsaturated aldehydes favor the formation of saturated aldehydes via the hydrogenation of the C=C bond while the manipulation of the kinetics of the process may yield the desired unsaturated alcohol product via the hydrogenation of the C=O bond. Most of the studies done on single metal surfaces using acrolein (CH_2=CH=CHO), the smallest of these aldehydes, show that the thermodynamically-preferred product (propanal) is always the favored product. However, bimetallic systems have been shown to possess unique properties, compared to their single metal counterparts, including novel reaction pathways. Thus, our aim is to study acrolein hydrogenation on a bimetallic Pt/Ru(001) system to determine if the presence of the Pt atoms can enhance the selectivity and activity towards the formation of the unsaturated alcohol (2-propenol).

In this initial study, temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS) were used to determine if the bare Ru(001) surface is active towards (partial and complete) hydrogenation of acrolein and if it's selective for the desired product (2-propenol). At low coverages, acrolein was found to adsorb on the surface, at 90 K, via the C=O bond and completely decomposes to CO(g) around 460 K. As the coverage increases, adsorption via the C=C bond predominates and most of the acrolein desorbs molecularly or decomposes to CO(g). However, some of the acrolein also self-hydrogenates to yield all the possible hydrogenation products – propanal, 2-propenol, and 1-propanol with TPD peak temperatures at 180, 210, and 280 K respectively – with propanal having the highest yield. Co-adsorption with H_2(g) enhances the adsorption via the C=C bond and the yield of all the products. These results will serve as a guide for the study on the Pt/Ru(001) system.

8:20am **HC+SS-ThM2 Dynamics of Formate Synthesis from CO_2 and Formate Decomposition on Cu Surfaces***, J. Quan, T. Kozarashi, T. Ogawa, T. Kondo, **Junji Nakamura**,* University of Tsukuba, Japan

Much attention has been paid to methanol synthesis by hydrogenation of CO_2 as a promising chemical conversion of CO_2. It has been well-known that Cu-based catalysts show high activity for the methanol synthesis, in which the initial elementary step of CO_2 is formation of formate species by the reaction of CO_2 with surface hydrogen atoms on Cu. Previous kinetic measurements of the formate synthesis by hydrogenation of CO_2 have suggested an Eley-Rideal (E-R) typed mechanism that CO_2 directly attacks a hydrogen atom on Cu surfaces. We have thus tried to prove the E-R typed mechanism by molecular beam experiments assuming that the reaction between incoming CO_2 molecules and Cu surfaces is thermally non-equilibrated. We first prepared hydrogen atoms on cold Cu(111), Cu(110), and Cu(100) kept around 200 K and then hot CO_2 molecular beams were illuminated onto the surfaces with controlling its vibrational and translational energy. It is found that the formate synthesis proceeds significantly without heating Cu samples if vibrational and translational energies are supplied to gaseous CO_2. The results clearly indicate the thermal non-equilibrium dynamics. Possibility of a tunneling mechanism between CO_2 and a hydrogen atom on Cu was discarded because no significant H/D effect was observed on the reaction rate of formate synthesis. On the other hand, we have studied the dynamics of the formate decomposition as a reverse reaction of the formate synthesis. We measured the angular distribution and the translational energy of desorbed CO_2 formed by the decomposition of formate on Cu(110) under a steady state reaction of HCOOH and O_2. The angular distribution showed a sharp collimation, $\cos^6\theta$, perpendicular to the surface. The translational energy of CO_2 was independent of the surface temperature of Cu(110). It is thus found that the formate decomposition is also thermal non-equilibrium dynamics. However, the translational energy was as low as 100 meV, which is much lower than that required for formate synthesis, about 600 meV. The discrepancy will be discussed in the presentation.

8:40am **HC+SS-ThM3 Step-Type Selective Oxidation on Pt Surfaces***, **Rachael Farber**,* Loyola University Chicago*; C. Badan,* Leiden Institute of Chemistry, The Netherlands*; H. Heyrich,* Leiden Institute of Chemistry*; L.B.F. Juurlink,* Leiden Institute of Chemistry, The Netherlands*; D.R. Killelea,* Loyola University Chicago

The development of predictive models of heterogeneously catalyzed systems relies on a sound understanding of the atomic-level details of the interactions of gas-phase species with the metal surface. A key factor in this tapestry is how the surface geometry influences reactivity. Single metal crystals with low Miller indices have often been used to probe the interactions between the reactive adsorbates and catalytic metal substrate. These low index surfaces are more accessible both computationally and experimentally, and have been essential to our current understanding of metal surface-catalyzed chemistry. However, the decreased complexity, because of the absence of active surface defects, can result in incomplete models of actual catalytic systems. Actual catalytic surfaces are believed to possess many defect sites that contribute to the overall reactivity of the catalyst. It has been recently shown that differences in the (110) and (100) step edge greatly influences water structures on the Pt surface. By using highly stepped Pt crystals with (110) and (100) steps, we see that the slight geometric differences between the (110) and (100) step also has profound effects on oxygen adsorption on stepped Pt crystals.

By utilizing highly stepped Pt crystals to study oxygen adsorption, along with ultra-high vacuum (UHV) surface science techniques such as temperature programmed desorption (TPD) and low temperature UHV scanning tunneling microscopy (STM), we are able to further understand O-Pt interactions on a surface that better mimics actual catalytic environments. Pt(553), with (110) step edges, was studied via STM to support the different behavior seen in oxygen adsorption between the (110) and (100) step edges in TPD experiments. The combination of TPD, STM, and variation in crystal step edge geometry allows for a more complete understanding of O_2 adsorption and dissociation on the Pt(553) surface and, more generally, (110) and (100) type step edges on Pt crystals.

9:00am **HC+SS-ThM4 Vibrational Symmetry Effects in the Dissociative Chemisorption of CH_2D_2 on Ni(111)***, **Arthur Utz**, N. Chen, E.H. High,* Tufts University

Vibrational state resolved reactivity measurements have established that mode-selective chemistry, in which the reaction probability, S_0, depends on the identity of the reactant's vibrational state, and bond selective chemistry, in which the product identity depends on the reagent's vibrational state, is widespread in the dissociation of methane and its isotopologues on Ni and Pt surfaces. Two factors lead to the observed mode- and bond-selectivity. First, methane's distorted transition state geometry introduces a bias that favors those vibrational motions that best access the transition state geometry. The sudden vector projection (SVP) model of Guo and coworkers predicts selectivity based on this factor. As the methane molecule approaches the surface, the molecule-surface interaction potential can also perturb the molecule's vibrations and lead to vibrational energy redistribution in the entrance channel for the reaction. Reaction path Hamiltonian calculations by Jackson and coworkers, quantum dynamics calculations by Kroes et al., and the vibrational adiabatic predictions of Halonen et al. focus on how this second factor impacts reactivity. In all of these calculations, the incident molecule's vibrational state symmetry can influence the vibrational coupling channels and energy flow pathways for the molecule as it approaches the surface.

This talk will focus on state-resolved experimental measurements of CH_2D_2 dissociation on a 90K Ni(111) surface. Unlike CH_4, the C_{2v} symmetry of the CH_2D_2 molecule results in both the v_1 symmetric- and v_6 antisymmetric C-H stretching vibrations being infrared active. Therefore, we can use state-resolved infrared laser excitation of CH_2D_2 in a supersonic molecular beam to measure the reaction probability for these two C-H stretching states as a function of incident translational energy (E_{trans}). By performing the measurements at 90K, we observe a sharp energy threshold for reaction that permits an unusually precise measure of the efficacy of each vibration in promoting reaction. Our choice of excitation transitions further reduces experimental error in comparing the two states' reactivity. Contrary to the predictions of a vibrationally adiabatic model, the two states have nearly identical reaction probability. We will compare these results with recent reaction path Hamiltonian calculations from the Jackson group to explore how the symmetry of these two vibrational states impacts their reactivity.

9:20am **HC+SS-ThM5 Elementary Steps in Surface Reactions: Mechanisms, Kinetics and Thermodynamics***, **Swetlana Schauermann**,* Christian-Albrechts-Universität Kiel, Germany **INVITED**

Atomistic–level understanding of surface processes is a key prerequisite for rational design of new catalytic and functional materials. In our studies, we investigate mechanisms, kinetics and thermodynamics of heterogeneously catalyzed reactions and adsorption processes on nanostructured model supported catalysts by combination of multi-molecular beam techniques, infrared reflection-absorption spectroscopy and single crystal adsorption calorimetry. By employing these methods under well-defined ultra high vacuum conditions, we study mechanistic details of complex multi-pathway surface reactions, such as hydrocarbon transformation in presence of hydrogen or selective hydrogenation of multi-unsaturated hydrocarbons. The ultimate goal of our research is obtaining detailed correlations between reactivity, selectivity and the particular structure of the catalytic surface.

Specifically, it will be shown that selective hydrogenation of the C=O bond in acrolein to form an unsaturated alcohol is possible over Pd(111) with nearly 100 % selectivity. However, this process requires a very distinct modification of the Pd(111) surface with an overlayer of oxopropyl spectator species that are formed from acrolein during the initial stages of reaction and turn the metal surface selective towards propenol formation.

In the second part, a mechanistic picture of interaction of water with model Fe_3O_4(111)/Pt(111) surface will be discussed. A combination of single crystal adsorption calorimetry and infrared spectroscopy was employed to determine the adsorption and dissociation heats of water and identify the surface species. We show that water dissociates readily on iron oxide surfaces forming a dimer-like hydroxyl-water complex and proved that the generally accepted model of water dissociation to two individual OH groups is incorrect.

11:00am **HC+SS-ThM10 CO_2 Hydrogenation on Rhodium: Comparative Study using Field Emission Techniques and 1-D Atom Probe***, **Sten Lambeets**,* Université Libre de Bruxelles, Belgium*; C. Barroo,* Harvard University*; S. Owczarek, N. Gilis,* Université Libre de Bruxelles, Belgium*; N. Kruse,* Washington State University*; T. Visart de Bocarmé,* Université Libre de Bruxelles, Belgium

Valorization of CO_2 into useful products is one way to fulfill current environmental and economic imperatives. This can be done via the selective reduction of CO_2 using heterogeneous catalysts. To get a better understanding of the fundamental processes, we studied the CO_2 adsorption as well as its interaction with H_2 on single nanosized Rh crystals. For this, Field Emission Microscopy (FEM), Field Ion Microscopy (FIM) and 1-D Atom Probe (1DAP) were used. These methods use samples prepared as sharp needles, the extremity of which is imaged with nanoscale (FEM) and even with atomic lateral resolution (FIM).

The structure of the Rh nanocrystals is characterized by FIM, and CO_2 adsorption, dissociation and hydrogenation is studied in FEM mode. The brightness intensity of the FEM pattern depends on the presence and the nature of adsorbates. Probing and analyzing the brightness signal over time allows to qualitatively monitor the variations of surface composition, and thus the presence of surface reactions, during the ongoing processes.

Finally, 1DAP, which corresponds to the combination of a FIM device with mass spectrometry, is used to identify the nature of the different surface species.

The FEM pattern of a clean sample essentially highlights {012} facets. During CO_2 exposure, the brightness of these facets drastically decreases and remains dark, reflecting the CO_2 dissociative adsorption over these facets - leading to the formation of O(ad) species. The presence of O(ad) at the surface induces a new FEM pattern where {113} facets become the most visible. This pattern reflects the formation of subsurface oxygen O(sub) beneath the {113} facets, which is confirmed by comparison with N_2O, O_2 and CO on Rh systems. To study the hydrogenation of CO_2, pure H_2 gas is introduced while the pressure of CO_2 is kept constant. Reaction phenomena, proved by variations in the brightness pattern, were observed from 650 to 734 K.

The adsorption of hydrogen at the surface leads to the formation of H(ad) species reacting with O(ad) to form H_2O(ad). Similar reaction phenomena were also observed with N_2O+H_2/Rh and O_2+H_2/Rh systems in the same temperature range, but not with the $CO+H_2$/Rh system, proving the role of O(ad) in the mechanism. Our observations allow to identify the reaction as the Reverse Water Gas Shift:

$CO_2(g)+H_2(g) \rightarrow CO(g)+H_2O(g)$

These assumptions are in line with direct local chemical first analyses performed by 1DAP. Rhodium oxides species - RhO^{2+} and RhO_2^{2+} - and CO_2 with its dissociation products, i.e. CO_2^+, CO^+ and O^+ , are detected in the first layers of a (115) facet of the Rh nanoparticle during an exposure to pure CO_2 at 325 K.

11:20am **HC+SS-ThM11 State-resolved Reactivity of Methane on Ir(110)-(1x2)***, **Eric Peterson**, E. Nicotera, E.K. Dombrowski, A.L. Utz,* Tufts University

The rate-limiting step in the steam reforming reaction, in which methane and water react to form hydrogen gas and carbon monoxide (syngas), is the initial cleavage of a C-H bond in the methane molecule. Methane's dissociative chemisorption is highly activated on catalytically active transition metal surfaces. To date, experimental measurements have focused on CH_4 molecules whose internal (vibrational) energy is less, and frequently much less than the threshold energy for reaction. Under those conditions, significant incident translational energy (TE) or energy transfer from the surface is required to activate dissociation, and reactions most often proceed via a direct dissociative chemisorption mechanism. Using a molecular beam in conjunction with an OPO-OPA continuous-wave IR laser, we are able to prepare methane molecules with a sharply defined kinetic energy and 36 kJ/mol of internal vibrational energy, which approaches or even exceeds the threshold energy for dissociative chemisorption. These molecules possess sufficient energy to react via direct or precursor-mediated mechanisms. The direct channel is characterized by an increase in reactivity with increasing TE, and is dominant for molecules with >10 kJ/mol of TE. Molecules with <10 kJ/mol of energy react through precursor-mediated channel, in which reactivity decreases with increasing TE. This low-TE precursor channel is especially interesting in a catalytic context, as most molecules under typical industrial reactor conditions have TEs where trapping, and therefore physisorption probabilities are high.

In studies of CH_4 dissociation on Ir single crystal surfaces, we observe both the precursor and direct channels for reaction. On Ir(111) we observe that 36 kJ/mol of E_{vib} in the n_3 C-H stretch enhances reactivity in both channels at a surface temperature of 1000K. On the corrugated Ir(110)-(1x2) surface, we still observe vibrational-energy enhancement in both channels, but the TE dependence of S_0 differs for the vibrationally hot and ground state CH_4 molecules at T_{surf} = 1000K. Upon lowering T_{surf} to 500K, vibrational ground state molecules no longer have a pronounced precursor-mediated reaction channel, but the vibrationally excited molecules do. We will discuss the origin of these similarities and differences. The observed reactivity of vibrationally hot methane molecules with thermal TE points to the potentially important role that vibrationally hot precursor molecules may play in industrially catalyzed reactors.

11:40am **HC+SS-ThM12 Curved Single Crystals As Tools to Study Structure Dependences in Surface Science and Gas-Surface Reactions Dynamics***, **Ludo Juurlink**,* Leiden University, Netherlands **INVITED**

The surface science approach has benefited for many decades from the availability of flat single crystal samples of high purity and high surface quality. The traditional flat, polished samples provide the user with a single surface structure that dominates over macroscopic length scales. However, a single sample that provides the user with multiple surface structures may provide additional benefits. For example, in attempts to relate chemical reactivity or selectivity to surface structure, having a continuous range of vicinal surfaces in a single sample can speed up scientific research and circumvent experimental difficulties. Also for studies focusing on either short or long-range effects in adsorbates and electronic states that are perturbed by steps, a single sample with a range of surface structures is an excellent tool. Therefore, we have revived the implementation of curved single crystal surfaces in traditional surface science studies and elaborated the implementation toward gas-surface reaction dynamics. Depending on the bulk crystal structure and the directions of the apex and curvature, many different surface structures are available in a single sample. We show how we now use LEED, AES, STM, TPD, RAIRS and supersonic molecular beam techniques to directly relate surface structure to molecular and dissociative adsorption, desorption, and chemical reactions. We exemplify the possibilities by showing recent results from studies that used a cylindrical Ni single crystal, two curved Ag samples, a Co curved sample and two Pt curved single crystal surfaces with various apex directions.

Surface Science
Room 104D - Session SS-ThM

Chirality and Enantioselectivity on Surfaces; Ionic Liquid Interfaces

Moderator: Eddy Tysoe, University of Wisconsin-Milwaukee

8:00am **SS-ThM1 Self-assembly and Dynamics for Chiral Conformational Switches on Surfaces Studied by UHV-STM***, **Trolle Linderoth**,* Aarhus University, Denmark **INVITED**

Chiral self-assembled structures formed from organic molecules adsorbed on surfaces can be studied at high resolution by Scanning Tunneling Microscopy under Ultra-High Vacuum conditions. Through collaboration between UHV-STM experiments and organic synthesis, we have investigated how molecular conformational flexibility can lead to new chiral effects in the form of chiral switching, chiral accommodation and chiral induction, allowing transfer of chirality from the molecular to the supra-molecular level [1-5]. To generalize these principles, we have recently developed a new system of 3-bit binary conformational switches (Oligo-Naphthalene Ethynylenes) [6, 7] and in particular quantified their dynamic conformational switching and collective effects in ordering using time-resolved STM movies.

[1] Weigelt, S.; Busse. C.; Petersen, L.; Rauls, E.; Hammer, B.; Gothelf, K.V.; Besenbacher, F.; Linderoth, T.R. Nature Materials, **2006**, **5** 11.

[2] Bombis, C.; Weigelt, S.; Knudsen, M. M.; Nørgaard, M.; Busse, C.; Lægsgaard, E.; Besenbacher, F.; Gothelf, K. V.; Linderoth, T. R. ACS NANO **2010** *4*, 297.

[3] Knudsen, M.; Kalashnyk, N.; Masini, F.; Cramer, J.; Lægsgaard, E.: Besenbacher, F.; Linderoth, T. R.; Gothelf, K. .V. Journ. Am. Chem. Soc. **2011**, *133*, 4896.

[4] Masini, F.; Kalashnyk, N.; Knudsen, M. M.; Cramer, J. R.; Lægsgaard, E.; Besenbacher, F.; Gothelf, K. V.; Linderoth, T. R. Journ. Am. Chem. Soc. **2011,***133* 13910.

[5] Nuermaimaiti, A.; Bombis, C.; Knudsen, M. M.,; Cramer, J.; Lægsgaard, E.; Besenbacher, F.; Gothelf, K. V.; Linderoth, T. R. ACS Nano **2014,***8*, 8074.

[6] Cramer, J. R.; Ning, Y.; Shen, C.; Nuermaimaiti, A.; Besenbacher, F.: Linderoth, T. R.; Gothelf, K.V. Eur. J. Org. Chem. **2013** 2813.

[7] Ning, Y.; Cramer, J. R.; Nuermaimaiti, A.; Svane, K.; Yu, M.; Lægsgaard, E.; Besenbacher, F.; Xue, Q.-K. ; Ma, X.; Hammer, B.; Gothelf, K. V.; Linderoth, T. R. J. Chem. Phys. **2015** *142*, 101922.

8:40am **SS-ThM3 Chiral Recognition among Non-planar Aromatic Hydrocarbons on Metal Surfaces***, A. Mairena,* Empa, Swiss Federal Laboratories for Materials Science and Technology*; M. Parschau, **Karl-Heinz Ernst**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Molecular recognition among chiral molecules on surfaces is of paramount importance in biomineralization, enantioselective heterogeneous catalysis, and for the separation of chiral molecules into their enantiomers via crystallization or chromatography. Understanding the principles of molecular recognition in general, however, is a difficult task and calls for investigation of appropriate model systems. One popular approach is thereby studying intermolecular interactions on well-defined solid surfaces, which allows in particular the use of scanning tunneling microscopy (STM). We present an elucidation of chiral recognition of helical and bowl-shaped hydrocarbons in monolayers and in multilayers. For penthalicene, a unique coexistence of 2D conglomerate and racemate is observed on a copper surface. Chiral bias in form of small enantiomeric excess leads to single enantiomorphism in multilayered samples of racemic heptahelicene.[1] Only the majority enantiomer is allowed to exist in the bottom layer, whereas the top layer consists exclusively of the minority enantiomer, i.e., enantioselective de-wetting occurs.

Pentagonal substituted chiral buckybowls form 2D racemate crystals, but chiral hemifullerene restructures a copper surface such that special chiral kinks become stabilized by the enantiomers.[2]

1 M. Parschau, K.-H. Ernst, *Angew. Chem. Int. Ed.* **2015**, *54*, 14422.

2 W. Xiao, K.-H. Ernst et al., *Nature Chemistry***2016**, in press.

9:00am **SS-ThM4 Competing Forces in Chiral Surface Chemistry: Enantiospecificity versus Enantiomer Disproportionation***, **Andrew Gellman**, Y. Yun,* Carnegie Mellon University

{The enantiospecific adsorption of chiral molecules on chiral surfaces is dictated by two competing forces the enantiospecificity of adsorption energetics and the propensity of enantiomers to disproportionate into homochiral (conglomerate) or heterochiral (racemate) clusters. These phenomena have been studied by measuring the surface enantiomeric excess, ee_s, of mixtures of chiral amino acids adsorbed on Cu surfaces and in equilibrium with gas phase mixtures of varying enantiomeric excess, ee_g. Alanine adsorption on Cu{3,1,17}$^{R\&S}$ surfaces is non-enantiospecific, $ee_s = ee_g$, because alanine enantiomers do not interact with either the surface or one another enantiospecifically. Aspartic acid adsorbs enantiospecifically on the Cu{3,1,17}$^{R\&S}$ surfaces; ee_snot= ee_g, even during exposure to a racemic mixture in the gas phase, ee_g=0. Exposure of the achiral Cu{111} surface to non-racemic aspartic acid, ee_g not= 0, results in local amplification of enantiomeric excess, $|ee_s| > |ee_g|$, as a result of homochiral disproportionation. Finally, in spite of the fact that the Cu{653}$^{R\&S}$ surfaces are chiral, the adsorption of aspartic acid mixture is dominated by homochiral disproportionation of adsorbed enantiomers rather than enantiospecific adsorbate-surface interactions, $|ee_s| > |ee_g|$. All of these types of behavior are captured by a Langmuir-like adsorption isotherm that also describes competition between enantiospecific adsorption and both homochiral (conglomerate) and heterochiral (racemate) clustering of adsorbed molecules.}

9:20am **SS-ThM5 Probing Individual Binding Sites around Individual Chiral Molecules on a Metal Surface: Chemisorption and Non-Covalent Bonding in Heterogeneous Asymmetric Hydrogenation***, **Peter McBreen**,* Laval University, Canada*; B. Hammer,* Aarhus University, Denmark*; M. Goves,* Aarhus University*; J.-C. Lemay, Y. Dong,* Laval University, Canada

There is rapid progress in the design and application of chirally-modified metal particles for heterogeneous catalytic enantioselective reactions. Modification is achieved by adsorbing chiral molecules to create asymmetric active sites. Great advances are being made in *operando* studies, surface science studies and theoretical studies of such systems. We will describe combined experimental and theoretical work related to the enantioselective hydrogenation of activated ketones on chirally-modified Pt(111). We will present results from combined variable temperature STM and optB88-vdW DFT studies of individual bimolecular docking complexes formed between enantiopure 1-(1-naphthyl)ethylamine, and related molecules, and representative prochiral substrates. The experiments reveal sub-molecularly resolved site-specific and stereospecific data. Single chemisorbed enanantiomers simultaneously present several chiral pockets, each displaying a specific prochiral ratio for a given substrate molecule. A hierarchy of chemisorption and intermolecular interactions is found to control prochiral selection at each pocket. Fine-tuning the structure of the modifier reveals how sensitive the stereochemical outcome is to even minor molecular changes. Time-lapsed STM measurements of individual substrate molecules sampling a set of chiral pockets provide new insight on stereocontrol, and on reaction paths and barriers at individual binding sites.

9:40am **SS-ThM6 Enhanced Hydrogenation Activity and Diastereomeric Inter-actions of Methyl Pyruvate Co-adsorbed with R-1-(1-Naphthylethylamine) on Pd(111)***, **Mausumi Mahapatra**, W.T. Tysoe,* University of Wisconsin-Milwaukee

The diastereomeric interactions and reactivity of co-adsorbed methyl pyruvate (MP) and *R*-1-(1-naphthyl)ethylamine (NEA) are studied on a Pd(111) model single crystal catalyst using temperature-programmed desorption (TPD) and scanning tunneling microscopy (STM) with the aim of identifying the nature of the interactions and understanding the observed enhancement in hydrogenation activity of MP to methyl lactate on NEA-modified surfaces. The enhancement in hydrogenation activity of chirally modified sites is critical in designing heterogeneous enantioselective catalysts by mitigating the effect of unmodified racemic sites. TPD experiments of coadsorbed MP and hydrogen or deuterium on Pd(111) reveal that NEA accelerates the rates of both MP hydrogenation and H/D exchange. The measured STM images of docking complexes on Pd(111) are classified according to the angles between the long axes of MP and the naphthyl ring of NEA, which fall into well-defined ranges of 10 ± 5, 45 ± 5 and 70 ± 5º. Docking structures are modeled using first-principles density functional theory (DFT) calculations that include van der Waals interactions, and STM image simulations. Excellent agreement is found both between the shapes of the calculated and simulated images and their theoretical and experimental dihedral angle distributions, thereby confirming the validity of the calculations. Diastereomeric interactions between NEA and MP occur predominantly by binding of the carbon-carbon double bond of the *enol* tautomer of MP to the surface, while simultaneously optimizing C=O····H_2N hydrogen-bonding interactions. The combination of chiral-NEA driven diastereomeric docking with a tautomeric preference enhances the hydrogenation activity since C=C bonds hydrogenate more easily than C=O bonds. This model provides a rationale for the catalytic observations.

11:00am **SS-ThM10 Structural Transitions of Ionic Liquids at Nanoconfined Interfaces***, **Rosa M. Espinosa-Marzal**,* University of Illinois at Urbana-Champaign **INVITED**

Ionic liquids (ILs) have remarkable properties including vanishingly low vapor-pressures, are non-flammable, and have wide thermal and electrochemical stability windows that make them ideal for several applications, including electrolytes in supercapacitors and lubricants. Our interest is to understand the interfacial behavior of ILs under nanoconfinement. Several studies have demonstrated the layered structure of ILs in nanoconfinement. The confined ions resist being " squeezed out" when surfaces are compressed, with the result that an IL film remains between the surfaces up to high pressures, thus preventing direct contact between the surfaces, also under shear, which can aid in reducing friction.

Laboratory studies have mainly focused on atomically flat and chemically homogeneous substrates, i.e. on ideal surfaces, to understand fundamental mechanisms. In our current work we are exploring the influence of nanoscale heterogeneities on ionic-liquid interfacial properties. Such heterogeneities can be composed of contamination, roughness or chemical surface groups. The strong molecular interactions still facilitate self-assembly of ILs on the surfaces, but they reveal new aspects of the IL behavior. We address diverse fundamental questions about the interfacial IL structure and the response to shear in the presence of heterogeneities. Further, these studies are of relevance to extend studies performed on ideal systems to real applications.

11:40am **SS-ThM12 Ionic Liquid Ordering at a Model Electrode Interface: 1-butyl-3-methylimidazolium Tetrafluoroborate, [C4C1Im][BF4], Interaction with the Anatase TiO2 (101) Surface***, **Michael Wagstaffe**,* University of Manchester, UK

Ionic liquids are room temperature molten salts comprised entirely of cations and anions. They have an array of unique physico-chemical properties that have led to their use in a wide variety of electrochemical systems.[1] These include actuators, corrosion inhibitors, energy storage for batteries, supercapacitors, displays and as the electrolyte in photovoltaic devices. Both the function and performance of devices employing ionic liquids are dependent on how the ionic liquid behaves at phase boundaries, interfaces and near interfacial areas. Previous studies have shown that ionic liquids have a tendency to self organize at the IL/solid interface.[2] Such ordering has been shown to reduce the barrier to charge injection when ionic liquids are used in oxide solar cells.[3] As such, the ordering and chemistry of ionic liquids at the anatase TiO_2(101) surface is of some interest since this is the dominant surface in mesoporous TiO_2 films used in dye sensitized solar cells.

Although there is a growing body of work on the surface chemistry of bulk ionic liquids studied by photoelectron spectroscopy, studies of their interaction with solid surfaces are still relatively rare. On this basis, in an attempt to address the gap in the work, we adopted a surface science approach in which we utilized a combination of X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. From this we were able to successfully determine the orientation of the cation on the surface of anatase(101), at both high and low coverage, and also the manner in which it adsorbs. Additionally, a surface induced degradation reaction of the anion was observed at room temperature.

[1] K. R. J. Lovelock *et al.Chem. Rev.*, 2010, **110**, 5158–90.

[2] E. Binetti *et al.J. Phys. Chem. C*, 2013, **117**, 12923–12929.

[3] B. R. Lee *et al. J. Mater. Chem.*, 2011, **21**, 2051.

12:00pm **SS-ThM13 In-Situ Photocurrent Measurements in Liquid-Phase Molecular Layer Deposition (LP-MLD)***, **Shi Bai,*** Tokyo University of Technology, Japan

[Introduction] A solution of the loss of heat by using black dye in a dye-sensitization solar cell is expending the width of the light absorbing wavelength by growing multi-dye with narrow wavelength to reduce the loss of heat. So, we supply and make the molecules grow according to the reaction between the molecules, and apply the multi-dye layer film by using Liquid-Phase Molecular Layer Deposition. By way of LP-MLD, the multi-dye layer forms on the surface of ZnO, and we test the expansion effect of the photocurrent spectrum width.

[Growth of multi-dye layer film]First, adsorb the p-type dye(Rose Bengal)molecules p1 on the surface. Because there is no reaction between the same molecules, and they don't combine each other. So the first layer is completed on the surface of the substrate which the surface is filled with p1.Second, remove the p1 by IPA(isopropyl alcohol), then supply the n1,molecules of n-type dye(Brilliant Green).p1 and n1 react and they combined. The same as step 1,the p1 layer is filled with n1,then the second layer is completed. Step 3 is using p-type dye(Eosin Y) molecules again. Repeat these steps, adsorb the molecules in the array as designed, and complete the multi-dye molecule layer film.

[Measurement of the photocurrent in LP-MLD]LP-MLD is a technology using the combination power between molecules of p-type dye and molecule of n-type dye to make a layer. Use IPA as the solvent to make a solution with the concentration of 1.6 x 10^{-2}mol/L. Set the substrate in a cell,inject the cell with IPA until the cell is full of it. Then inject the solution of p1 to make the dye molecules adsorbed by the substrate. After 20 minutes, in order to remove p1 solution in the cell, inject the cell with IPA again. After putting the laser on the substrate and measuring the photocurrent, repeat the process with other dye solution. Base on the measurement, the expansion effect of the photocurrent spectrum width was deduced.

Electronic Materials and Photonics
Room 102A - Session EM+SS+TF-ThA
Materials and Interfaces for Energy Storage

Moderators: Michelle Paquette, University of Missouri-Kansas City, Lee Walsh, University of Texas at Dallas

2:20pm **EM+SS+TF-ThA1 Strain Engineering of Ultrathin Metal Oxide Coatings Deposited using Atomic Layer Deposition for Controlled Electrochemical Energy Storage**, ***Nitin Muralidharan***, *R.E. Carter, A.P. Cohn, L. Oakes, C.L. Pint,* Vanderbilt University

Strain engineering has transformed applications in the semiconductor electronics industry, but has not been widely explored as a tool for electrochemical applications. Here we study the role of strain on the electrochemistry of metal oxide coatings deposited using atomic layer deposition onto super-elastic NiTi alloy surfaces. Specifically, we focus on vanadium pentoxide (V_2O_5) due to its well-known capability to function as a cathode for the intercalation of lithium ions. Exploiting the capability of NiTi to “lock-in” strain in the elastic regime, which extends up to ~ 15% strain, we study the correlation between strain transferred to the V_2O_5 active material and the electrochemical performance during lithium intercalation. Overall, our results indicate that pre-straining the material changes both the kinetics and energetics for intercalation properties. Furthermore, the diffusion coefficient of lithium ions in the V_2O_5 lattice can be effectively doubled through the application of elastic strains as low as ~0.25%. These results provide a route to controllably engineer bulk materials using principles of mechanics to improve battery or other electrochemical application performance.

2:40pm **EM+SS+TF-ThA2 Probing Li-Ion Transport in All-Solid-State Batteries through Electron Transparent Electrodes**, ***Alexander Yulaev,*** Center for Nanoscale Science and Technology, NIST, Gaithersburg, MD, USA; *A.A. Talin,* Sandia National Laboratories; *M.S. Leite,* University of Maryland; *A. Kolmakov,* NIST/CNST

All-solid-state batteries demonstrate a high power-to-weight ratio and high energy density, offering prospective opportunities for miniaturized micro-electronics and medical devices. Moreover, solid state batteries reduce the safety risk of thermal runaway that may occur in electrochemical cells with liquid electrolytes. In spite of growing interests, the details of lithium transport in solid electrolytes and their interfaces are not yet well understood due to a scarcity of experimental methods to probe electrochemical processes at the nanoscale. For instance, the factors controlling the rate and reversibility of Li ion intercalation are still an active area of research. Here we apply a combination of optical and scanning electron microscopies to resolve spatially Li-ion transport across a thin LiPON electrolyte. Using lithographically patterned electrodes, we monitor Li-ion transport through optically and electron transparent ultrathin anodes made either of high capacity silicon or carbon. The variation of the probing depth is achieved by altering the energy of the primary electron beam from 1 keV to 15 keV. Analogous to SEM tomography, the sequence of depth dependent 2D images can be employed to reconstruct the 3D diffusion pathways of Li ions in the electrolyte. In addition, we investigate Li plating/intercalation reactions, which occur at the anode-electrolyte interface during charge/discharge cycles. We foresee that this approach will help elucidate the effects of chemical and ion transport inhomogeneity inside the electrolyte and electrodes on the overall performance of the battery.

3:00pm **EM+SS+TF-ThA3 Thin Film Battery Materials for Fundamental Studies and Applications**, ***Nancy Dudney***, *K. Kercher, M. Veith,* Oak Ridge National Laboratory **INVITED**

Although most commercial rechargeable batteries are prepared by bulk and powder processing methods, vapor deposition of materials has led to important advances for fundamental research, modification of battery materials and interfaces, and also for commercialization of thin film batteries. Each of these areas will be illustrated with our studies of thin film materials for electrolyte, anode, and cathode components of rechargeable lithium and lithium-ion batteries with both planar and 3-dimensional architectures.

Acknowledgement: This work was supported by the U. S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division.

4:00pm **EM+SS+TF-ThA6 Silicon Compatible Pseudocapacitors Based on Nickel Hydroxide Functionalization of Carbonized Porous Silicon**, ***Joshua Fain***, *J.W. Mares, S.M. Weiss,* Vanderbilt University

We report on silicon (Si) compatible energy-storage supercapacitors (SCs) that incorporate pseudocapacitive nickel hydroxide [$Ni(OH)_2$] coupled with an electric double layer capacitance (EDLC) contributed by constituent $Ni(OH)_2$ and carbon layers. SCs can charge and discharge their energy much more rapidly than conventional batteries (within a few seconds to minutes), while possessing a higher energy storage capability than traditional capacitors (specific capacitances can reach thousands of F/g). Although SCs have made a commercial impact in regenerative breaking, there remains untapped potential for this technology in on-chip energy storage that could lead to reduced size and weight of microelectronic devices. However, advancements in Si-based on-chip energy storage has been hindered due to the rapid corrosion of Si by most electrolytes necessary for energy storage. Recently, it has been shown that conformal carbonization of high surface area porous silicon (PSi) electrodes protects the Si matrix from corrosion while also contributing to energy-storage EDLC behavior. Here, we show that functionalization of carbonized PSi with pseudocapacitive $Ni(OH)_2$ leads to significantly improved energy-storage capabilities of the SC electrode from a few to over 100F/g (with respect to the mass of the entire electrode), and up to 1400 F/g (with respect to the mass of only the $Ni(OH)_2$ - corrected for EDL contribution of the carbon). The electrodes were fabricated by electrochemical etching of PSi, followed by carbonization using chemical vapor deposition, and finally inclusion of $Ni(OH)_2$ into the matrix via a sol-gel process or electrochemical deposition. Cyclic voltammetry (CV) and charge/discharge experiments were carried out to investigate the energy storage capabilities of composite pseudocapacitive electrodes prepared with varying sol-gel concentrations and different electrochemical deposition parameters. Scan rates of 1-50 mV/s were used. Clear oxidation and reduction peaks were evident in the CV curves along with the EDLC contribution. We observed a tradeoff between specific surface area and $Ni(OH)_2$ quantity: the higher the $Ni(OH)_2$ coverage in the PSi matrix, the lower the accessible surface area. The highest specific capacitance of 1400 F/g was measured on an electrode with a modest concentration of $Ni(OH)_2$ (5 mg/mL nickel acetate tetrahydrate:2-methoxyethanol) at 50 mV/s. The results of these studies suggest that PSi is an excellent high surface area host template for $Ni(OH)_2$ that enables high specific capacitance to be achieved on a Si-compatible platform that could be directly integrated into microelectronic devices.

4:20pm **EM+SS+TF-ThA7 In-situ Raman of Sodium Ion Cointercalation into Highly Crystalline Few-Layered Graphene**, ***Adam Cohn,*** *C.L. Pint,* Vanderbilt University

A maximum sodium capacity of ~ 35 mAh/g has restricted the use of crystalline carbon for sodium ion battery anodes. We demonstrate that a diglyme solvent shell encapsulating a sodium ion acts as a “non-stick” coating to facilitate rapid ion insertion into crystalline few-layer graphene and bypass slow desolvation kinetics. This yields storage capacities above 150 mAh/g, cycling performance with negligible capacity fade over 8000 cycles, and ~ 100 mAh/g capacities maintained at currents of 30 A/g (~ 12 second charge). Raman spectroscopy elucidates the ordered, but non-destructive cointercalation mechanism that differs from desolvated ion intercalation processes. In-situ Raman measurements identify the Na+ staging sequence and isolates Fermi energies for the first and second stage ternary intercalation compounds at ~ 0.8 eV and ~ 1.2 eV.

4:40pm **EM+SS+TF-ThA8 Using X-ray Reflectivity to Measure the Vacuum Ultraviolet Absorption Spectrum in Low-k Dielectrics**, ***Faraz Choudhury***, *H.M. Nguyen, W. Li,* University of Wisconsin-Madison; *Y. Nishi,* Stanford University; *J.L. Shohet,* University of Wisconsin-Madison

During plasma processing, low-k dielectrics are exposed to high levels of vacuum ultraviolet (VUV) radiation that can cause severe damage to the dielectric material. The degree and nature of VUV-induced damage depends on the VUV photon energies.[1] In this work, we determine the VUV absorption spectrum of low-k organosilicate glass (OSG) using specular X-ray reflectivity (XRR). Low-k SiCOH films were exposed to synchrotron VUV radiation with energies ranging from 7 to 25 eV and the electron density depth profile of the VUV irradiated films were extracted from the fitting of the XRR experimental data using the Parratt method. The results show that the depth of the VUV induced damage layer is sensitive to the photon energy. Between 7 to 11 eV, the depth of the damaged layer decreases sharply from 110 nm to 60 nm and then gradually increases to 85 nm at 21 eV. The maximum VUV absorption in low-k films occurs between 11 and 15 eV. This method is also utilized to investigate the penetration depth of 5 to 25 eV photons in porous SiCOH films with porosities ranging from 15 to 50%. It is seen that the penetration depth of photons increases with porosity. This work shows that XRR electron density depth profiling can be a very effective, non-destructive tool to determine the penetration depth and absorption coefficients of photons and other reactive species from a plasma in various kinds of dielectric films.

This work was supported by the Semiconductor Research Corporation under Contract 2012-KJ-2359

[1] T. V. Rakhimova et al, J. Phys. D: Appl. Phys. 47 (2014) 025102

5:00pm **EM+SS+TF-ThA9 On-chip [18F]fluoride Concentration for Microfluidic PET Tracer Synthesis***, **Xin Zhang**, J. Buck, M. Nickels, C. Manning, L. Bellan,* Vanderbilt University

Positron emission tomography (PET) is a valuable medical imaging method that relies on radioactive tracers that target specific sites in the body. Development of these tracers is currently hindered by the enormous infrastructure requirements to perform the necessary radioisotope production and subsequent reactions. To overcome this hurdle and facilitate PET tracer development, we are designing simple, modular microfluidic systems that support on-chip radiosynthesis reactions with small volumes of reagents. In this work, [^{18}F]fluoride (a positron emitter widely used in PET imaging due to its convenient half-life of 110 minutes) is concentrated with a miniaturized anion exchange column located in a microfluidic device fabricated in polydimethylsiloxane (PDMS). By employing a microfluidic device, we aim to achieve more controlled diffusion and reactive kinetics. Instead of relying on complicated flow control elements (e.g. valves), in this microfluidic system, a channel containing pillars with a spacing less than the average diameter of the anion exchange beads is used to trap relatively monodispersed, rigid polystyrene/divinyl benzene beads. We characterized the ability of this miniaturized on-chip exchange column to capture and release quantities of [^{18}F]fluoride appropriate for human imaging (a typical dose is 10 mCi).

Our device is composed of a main chamber with larger microchannels (9 mm long) connected to an inlet and outlet. A laser writer (Heidelberg µPG 101) was used to create patterns on a silicon wafer using a 60 µm thick layerof mr-DWL resist; this template was subsequently used to pattern a microfluidic structure in PDMS. The desired quantity (2.9 mL) of anion exchange beads was trapped by a double row of square pillars near the outlet of the chamber, and the beads subsequently activated with 1.0 M of $KHCO_3$. Diluted [^{18}F]fluoride (100 mCi/mL) sourced from a nearby cyclotron was introduced into the system using a syringe pump, flowing at 0.05 mL/min for 10 minutes.

By quantifying the radioactivity of the [^{18}F]fluoride introduced, the radioactivity of the chip, and the radioactivity of the outflow, we could determine trapping and release efficiency. We observed near complete capture of [^{18}F]fluoride (50 mCi)on our chips in a relatively short time. Moreover, elution with a small volume (less than 200 mL) of Kryptofix (K_{222})/K_2CO_3 was able to release nearly all the [^{18}F]fluoride (49 mCi). Thus, this device is capable of simply and efficiently trapping [^{18}F]fluoride and controllably releasing the concentrated radiolabel in small volumes for downstream reaction with desired molecules.

5:40pm **EM+SS+TF-ThA11 The Role of Electron-Beam Deposition Rate in Controlling Properties of the Titanium/Semiconductor Interface***, **Keren Freedy**, A. Giri, B.M. Foley,* University of Virginia*; J. Bogan, R. O'Conner,* Dublin City University, Ireland*; P.E. Hopkins, S. McDonnell,* University of Virginia

Electron beam evaporation under high vacuum is very widely used for contact deposition in electronic device fabrication. Ti has a low work function and is commonly deposited as a contact or adhesion layer for other metals in silicon-based devices and more recently in 2D semiconductors. Previous work on Ti/MoS_2 contacts suggests that electron beam evaporation of Ti under high vacuum results in the formation of TiO_2 at the interface while UHV deposition results in unintentional reactions between metallic Ti and the MoS_2 substrate (McDonnell et al., 10.1021/acsami.6b00275). Since the majority of reports using Ti as a contact metal utilize HV rather than UHV e-beam processes, understanding the role of process conditions on the properties of this contact/semiconductor interface is of the utmost importance. To avoid the large variability observed in metal/MoS_2 contacts, we focus on Si as a case study to investigate the thermal and electronic properties of the Ti/semiconductor interface. The present study examines the effect of deposition rate on the properties of the Ti/Si interface. Electron beam evaporation of Ti onto both hydrogen-terminated and native oxide (001) Si surfaces is performed at varied deposition rates ranging from 0.1 to 5 A/s at pressures of ~10^{-6} Torr. Prior to ex-situ characterization, the samples are capped with Au in the evaporator to prevent further oxidation in air. Photoelectron spectroscopy measurements reveal that oxide composition is inversely proportional to the deposition rate. X-ray diffraction data shows no evidence of metallic Ti at slower deposition rates. Due to an appreciable partial pressure of O_2 at high vacuum, the composition of the deposited material is sensitive to the impingement rate of Ti on the surface. It follows that higher deposition rates should result in a smaller fraction of oxide phases. Electron and phonon transport across the interface will be studied as a function of deposition rate.

6:00pm **EM+SS+TF-ThA12 Single Crystal Study of Layered U_nRhIn_{3n+2} Materials: Case of the Novel U_2RhIn_8 Compound***, **Attila Bartha**, M. Kratochvílová,* Charles University, Czech Republic*; M. Dušek,* Institute of Physics ASCR, Czech Republic*; M. Diviš, J. Custers, V. Sechovský,* Charles University, Czech Republic

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

The role of dimensionality in *f*-electron systems has been mainly discussed in the context of quantum phase transitions and related phenomena. The series $Ce_nT_mIn_{3n+2m}$ (n = 1, 2; m = 0, 1, 2; T = transition metal) of layered compounds has been extensively investigated. $CeIn_3$ is cubic (3D) and orders antiferromagnetically (AFM) at T_N = 10.2 K. Under hydrostatic pressure superconductivity appears with highest T_c = 0.3 K at p = 2.5 GPa. In $CeRhIn_5$, the anisotropic crystal structure leads to a quasi-2D electronic and magnetic structure. The AFM order is reduced (T_N = 3.8 K) while superconductivity is supported, T_c increases to 1.9 K at p = 1.77 GPa.

We report on the properties of the novel U_2RhIn_8 compound studied the single crystal form in the context of parent $URhIn_5$ and UIn_3 systems [1]. The compounds were prepared by In self-flux method. U_2RhIn_8 adopts the Ho_2CoGa_8-type structure with lattice parameters a = 4.6056(6) Å and c = 11.9911(15) Å. The behavior of U_2RhIn_8 strongly resembles features of related $URhIn_5$ and UIn_3 with respect to magnetization, specific heat, and resistivity, except for magnetocrystalline anisotropy developing with lowering dimensionality in the series UIn_3 vs. U_2RhIn_8 and $URhIn_5$. U_2RhIn_8 orders AFM below T_N = 117 K and exhibits slightly enhanced Sommerfeld coefficient γ = 47 mJ.mol^{-1}.K^{-2}. Magnetic field leaves the value of Néel temperature for both $URhIn_5$ and U_2RhIn_8 unaffected up to 9 T. On the other hand, T_N increases with applying hydrostatic pressure up to 3.2 GPa. Results of thermal expansion measurement will be discussed in the framework of Ehrenfest relations. The character of uranium 5*f* electron states of U_2RhIn_8 was studied by first principles calculations based on the density functional theory combined with the Hubbard model. The overall phase diagram of U_2RhIn_8 is discussed in the context of magnetism in related UTX_5 and UX_3 (T = transition metal, X = In, Ga) compounds.

[1] A. Bartha *et al.*, J. Magn. Magn. Mater. 381 (2015) 310-315

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 103A - Session HC+SS-ThA

Advances in Theoretical Models and Simulations of Heterogeneously-catalyzed Reactions

Moderator: Donna Chen, University of South Carolina

2:20pm **HC+SS-ThA1 Theoretical Pathways to Predict (meta-)stability of Gas Phase Metal Oxide Clusters: Beyond the Static Mono-Structure Description***, **Saswata Bhattacharya**,* Indian Institute of Technology Delhi, India*; L.M. Ghiringhelli,* Fritz-Haber-Institut der Max-Planck-Gesellschaft*; N. Marom,* Tulane University

This talk is driven by the vision of computational design of cluster-based nanocatalysts. The discovery of the extraordinary activity in catalysis exhibited by small metal-oxide clusters has stimulated considerable research interest. However, in heterogeneous catalysis, materials property changes under operational environment (e.g. temperature (T) and pressure

(p) in an atmosphere of reactive molecules). Therefore, a solid theoretical understanding at a realistic (T, p) is essential in order to address the underlying phenomena. In this talk, I shall first introduce a robust methodological approach that integrates various levels of theories combined into one multi-scale simulation to address this problem[1]. I shall show one application of this methodology in addressing (T, p) dependence of the composition, structure, and stability of metal oxide clusters in a reactive atmosphere at thermodynamic equilibrium using a model system that is relevant for many practical applications: free metal (Mg) clusters in an oxygen atmosphere[2].

More recently, I have extended this development in designing clusters with desired properties. The novelty of this implementation is that it goes beyond the interpretation of experimental observations and addresses the challenging "inverse problem" of computationally designing clusters with target properties. The methodology is applied and thoroughly benchmarked on $(TiO_2)_n$ clusters [n=2, 3,...., 10, 15, 20][3]. All the results are duly validated using the highest level of theories currently achievable within Density Functional Theory (DFT).

References:

[1] S. Bhattacharya, S. Levchenko, L. Ghiringhelli, M. Scheffler, New J. Phys. 16, 123016 (2014).

[2] S. Bhattacharya, S. Levchenko, L. Ghiringhelli, M. Scheffler, Phys. Rev. Lett. 111, 135501 (2013).

[3] S. Bhattacharya, B. Sonin, C. Jumonville, L. Ghiringhelli, N. Marom, Phys. Rev. B 91, 241115 (R), (2015).

2:40pm **HC+SS-ThA2 Role of Oxygen at the Surface and Subsurface during Catalytic Oxidation by Silver*, Sharani Roy,*** University of Tennessee

Catalytic oxidation by the silver surface is used in several important industrial processes, such as epoxidation of ethylene to form polyethylene or partial oxidation of methane to form methanol. To understand the mechanisms of catalytic oxidation at the molecular level, it is essential to understand the interactions of atomic oxygen with the silver surface. We present a detailed theoretical study of oxygen adsorbed on the surface and subsurface of silver based on density functional theory and molecular dynamics simulations. Our ultimate goal is to develop a conceptual model of reactivity of surface oxygen and subsurface oxygen in catalytic oxidation by the silver surface. While the detailed quantum chemical calculations serve to accurately model the ground-state potential energy landscape of the oxygen-silver system, molecular dynamics simulates the motion of oxygen on the surface and subsurface at realistic laboratory or catalytic temperatures. We focus on several important phenomena, including surface-site preference, coverage dependence, and temperature dependence of oxygen adsorption at the surface and subsurface. We also investigate the changes in the surface structure of silver induced by the presence of oxygen. Due to the differences in structure, interatomic spacing, and binding sites of the (111) and (110) faces of the silver crystal, the adsorption properties of atomic oxygen vary for the two surfaces. Our study determines some fundamental differences in silver-oxygen interactions on the two surfaces, and provides qualitative insight on how the choice of surface can affect the participation of surface and subsurface oxygen in catalytic oxidation by silver. Future work will explore the interactions of surface oxygen and subsurface oxygen with reactant molecules such as methane or ethylene.

3:00pm **HC+SS-ThA3 Using Theory and Computation to Understand Plasma Enhanced Dry Reforming on Nickel Catalysts*, George Schatz,*** Northwestern University **INVITED**

Dry reforming is a process wherein CH_4 and CO_2 react to give synthesis gas and/or liquid fuels. Dry reforming is normally done under high temperature and pressure conditions, with a Ni catalyst, however it has recently been discovered that if a plasma is also present near the catalyst, then it is possible to get this reaction to go under modest conditions close to room temperature and atmospheric pressure. The role of the plasma in this process is poorly understood. In this talk I will describe several electronic structure studies that my group is doing which are designed to describe the processes involved in plasma enhanced dry reforming, including both the role of the plasma, and the gas-surface chemistry that occurs in the presence of plasma species. The plasma is known to fragment the reacting gases, especially CH_4, so we will study the interaction of methane fragments with various Ni surfaces, to show how this enhances chemisorption, surface dissociation, and subsequent reaction with species already on the surface. A highlight of this work involves the reaction of subsurface hydrogen with adsorbed CO_2 to give CO, water and other products. We have also studied the influence and ions and electrons on surface chemistry.

4:00pm **HC+SS-ThA6 The Impact of Structure on the Catalytic Behavior of Cu_2O Supported Pt Atoms*, Andrew Therrien*[*]**, Tufts University Department of Chemistry*; E.C.H. Sykes,* Tufts University

Single site catalysts composed of individual atoms on various oxide supports have been a major research focus in recent years. Such catalysts exhibit novel reactivity with the benefit of 100% atom efficiency and a dramatic reduction in the precious metal loading. However, despite several experimental examples of efficient single atom catalysts, there is much debate regarding the structure and catalytic mechanisms of such catalysts and debate over whether single atoms or nanoparticles are the active species. Given the complexity of heterogeneous catalysts and the size scale of the active sites, there is a need for a surface science and microscopy approach to understand the structure and reactivity of atomically dispersed atoms on oxides.

We have studied the structure and reactivity of individual Pt atoms supported on oxidized Cu using scanning tunneling microscopy (STM) and temperature programmed reaction (TPR). We first elucidated the structure of the support, a previously observed but unsolved Cu_2O overlayer on Cu, by density functional theory (DFT) and comparison of simulated STM images with experimental STM. We discovered that the oxide surface is inert towards CO oxidation, while the single Pt atom decorated surface is efficient for low-temperature CO oxidation. This system is also capable of water activation. Our combination of TPR and STM studies suggest that single Pt atoms supported on the oxide are indeed catalytically active and may be a good catalyst for the water-gas shift reaction.

4:20pm **HC+SS-ThA7 Energetics of Water Dissociative Adsorption on NiO(111)-2x2*, Wei Zhao***, University of Washington*; M. Bajdich,* Stanford University*; S. Carey,* University of Washington*; M. Hoffmann, A. Vojvodic, J. Nørskov,* Stanford University*; C.T. Campbell,* University of Washington

The energetics of the reactions of water with metal oxide surfaces are of tremendous interest for catalysis and electrocatalysis, yet the energy for the dissociative adsorption of water was only previously known on one well-defined oxide surface, $Fe_3O_4(111)$.[1] Here we report the first calorimetric measurement of the heat of reaction for the dissociative adsorption of water on NiO(111)-2x2 as a function of coverage, showing that the heat of dissociative adsorption decreases with coverage from 177 kJ/mol to 119 kJ/mol in the first 0.25 ML of coverage. These measurements provide an important benchmark for validating computational estimates of adsorption energies of molecular fragments on correlated metal-oxide such as NiO and for oxide surface chemistry in general, which is more challenging in this respect than for metal or wide-gap semiconductor surfaces. We also present DFT calculations of the energetics of this reaction, and compare it to the calorimetric results.

[1] P. Dementyev, K.-H. Dostert, F. Ivars-Barceló, C.P. O'Brien, F. Mirabella, S. Schauermann, X. Li, J. Paier, J. Sauer, H.-J. Freund, Water Interaction with Iron Oxides, Angewandte Chemie International Edition, 54 (2015) 13942-13946.

4:40pm **HC+SS-ThA8 Challenges in the First-Principles Description of Reactions in Electrocatalysis*, Axel Groß,*** Ulm University, Germany **INVITED**

In spite of its technological relevance in the energy conversion and storage, our knowledge about the microscopic structure of electrochemical electrode-electrolyte interfaces and electrical double layers is still rather limited. The theoretical description of these interfaces from first principles is hampered by three facts. i) In electrochemistry, structures and properties of the electrode-electrolyte interfaces are governed by the electrode potential which adds considerable complexity to the theoretical treatment since charged surfaces have to be considered. ii) The theoretical treatment of processes at solid-liquid interfaces includes a proper description of the liquid which requires to determine free energies instead of just total energies. This means that computationally expensive statistical averages have to be performed. iii) Electronic structure methods based on density functional theory (DFT) combine numerical efficiency with a satisfactory accuracy. However, there are severe shortcomings of the DFT description of liquids, in particular water, using current functionals.

Despite these obstacles, there has already significant progress been made in the first-principles modeling of electrochemical electrode-electrolyte interfaces. In this contribution, I will in particular focus on how the electrochemical environment can be appropriately taken into account

---

[*] **Morton S. Traum Award Finalist**

using numerically efficient schemes. In the presence of an aqueous electrolyte, metal electrodes are in general covered by either cations or anions. Based on the concept of the computational hydrogen electrode, the equilibrium coverage of Pt(111) with hydrogen (1,2) and halides (3) as a function of the electrode potential has been derived showing that halide and hydrogen adsorption is competitive, in agreement with experimental findings. The presence of the aqueous electrolyte has been taken into account modeling water layers either implicitly through a polarizable medium (2) or explicitly in ab initio molecular dynamics runs (3). To obtain a proper description of the water-water and the water-metal interaction, it turns out that the consideration of dispersion corrections is essential (4). The importance of the electrochemical environment in electrocatalytic processes will be demonstrated using the methanol electrooxidation on Pt(111) (5) as an example.

References

(1) S. Sakong, M. Naderian, K. Mathew, R. G. Hennig, and A. Gross, J. Chem. Phys. **142**, 234107 (2015).

(2) T. Roman and A. Gross, Catal. Today. **202**, 183 (2013).

(3) F. Gossenberger, T. Roman, and A. Gross, Surf. Sci. **631**, 17 (2015).

(4) K. Konigold and A. Gross, J. Comput. Chem. **33**, 695(2012).

(5) S. Sakong and A. Gross, submitted.

5:20pm **HC+SS-ThA10 Beyond the 2D Lattice Gas and 2D Ideal Gas Models for Adsorbates: The Hindered Translator / Hindered Rotor Model*, Liney Arnadottir*,** *L.H. Sprowl,* Oregon State University*; C.T. Campbell,* University of Washington

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. In such calculations, adsorbates are usually treated within either the 2D lattice gas or 2D ideal gas approximation to estimate their partition functions and entropies. Here we present a fast new method to estimate the partition functions and entropies of adsorbates that is much more accurate than those approximations, and recognizes the true oscillating nature of the adsorbate's potential energy for motions parallel to the surface. As with previous approaches, it uses the harmonic oscillator (HO) approximation for most of the modes of motion of the adsorbate. However, it uses hindered translator and hindered rotor models for the three adsorbate modes associated with motions parallel to the surface, and evaluates these using an approach based on a method that has proven accurate in modeling the internal hindered rotations of gas molecules. The translational and rotational contributions to the entropy of a hindered translator / hindered rotor calculated with this new method are, in general, very closely approximated (to within <0.25R error per mode) by the corresponding harmonic oscillator (i.e., 2D lattice gas) entropy when kT is less than the barrier. When kT exceeds the barrier, the hindered translator / hindered rotor model is closely approximated (to within 0.1 R) by the entropy of an ideal 2D gas. The harmonic oscillator / lattice gas model severely overestimates the entropy when kT greatly exceeds the barrier. The cutoff between the temperature ranges of applicability of these simple two approximations is very sharp but with our combined hindered rotor/hindered translator approach the whole temperature range is covered with the same approach.

5:40pm **HC+SS-ThA11 Methanol Partial Oxidation Catalyzed by Singly-dispersed Pd on ZnO(101¯0)*, Takat B. Rawal*[*]**, *S.R. Acharya, S. Hong, T.S. Rahman,* University of Central Florida

Heterogeneous catalysis by singly-dispersed metal atoms on non-metallic surfaces offers great potential for maximizing the efficiency of metal atoms, and optimizing their activity and selectivity. Herein, we present results from our *ab-initio* density functional theory (DFT) calculations for methanol partial oxidation (MPO), an industrially important reaction for the production of H_2, on Pd_1/ZnO(101¯0). To begin with we find that the Pd atom prefers to adsorb at the oxygen vacancy site i.e. the anion vacancy is responsible for stabilizing singly-dispersed Pd atom on ZnO(101¯0). We discuss the adsorption characteristics of a set of gas molecules (CH3OH, O_2, CO, CO_2, H_2O, H_2), and the potential energy profile including activation barriers for the reaction processes associated with MPO on Pd_1/ZnO(101¯0), and compare them with those on Pd16Zn16 nanoparticle and pristine ZnO(101¯0). We find that the singly dispersed Pd sites offer a high activity towards the formation of CO_2 and H_2 over that of CO and H_2O. We trace this reactivity to the electronic structure of the single Pd site as modified by its local environment which in turn facilitates a strong binding of CO to the Pd site, thereby increasing the CO desorption barrier and stabilizing O_2 on ZnO(101¯0), which is essential for further oxidation steps. With activation energy barriers and pre-exponential factors calculated from DFT, for a large set of reaction intermediates, we perform kinetic Monte Carlo simulations to determine the turn over frequencies and rate limiting steps in the formation of CO_2 and H_2 on Pd1/ZnO(101¯0), under ambient conditions.

Work supported in part by DOE grant DE-FG02-07ER15842.

6:00pm **HC+SS-ThA12 Simulations of Surface Induced Dissociation, Soft Landing, and Reactive Landing in Collisions of Protonated Peptide Ions with Organic Surfaces*, William Hase*,** *S. Pratihar,* Texas Tech University

Chemical dynamics simulations have been performed to explore the atomistic dynamics of collisions of protonated peptide ions, peptide-H^+, with organic surfaces. Overall, the results of the simulations are in quite good agreement with experiment. The simulations have investigated the energy transfer and fragmentation dynamics for peptide-H^+ surface-induced dissociation (SID), peptide-H^+ physisorption on the surface, soft landing (SL), and peptide-H^+ reaction with the surface, reactive landing (RL). The primary structure of biological ions is determined by SID, as well as information regarding the ions' fragmentation pathways and energetics. SID occurs by two mechanisms. One is a traditional mechanism in which peptide-H^+ is vibrationally excited by its collision with the surface and then dissociates in accord with the statistical, RRKM unimolecular rate theory after it rebounds off the surface. For the other mechanism, the ion *shatters* via a non-statistical mechanism as it collides with the surface. The simulations have also provided important dynamical insight regarding SL and RL of biological ions on surfaces. SL and RL have a broad range of important applications including preparation of protein and peptide microarrays. The simulations indicate that SL occurs via multiple mechanisms consisting of peptide-H^+ physisorption on and penetration in the surface. An important RL mechanism is intact deposition of peptide-H^+ on the surface.

Surface Science
Room 103C - Session SS+AS-ThA

Celebrating a Life in Surface Science: A Symposium in Honor of JOHN T. YATES, JR.

Moderators: John Russell, Jr., Naval Research Laboratory, Vincent Smentkowski, General Electric Global Research Center

2:20pm **SS+AS-ThA1 Introductory Remarks About Prof. John T Yates Jr. and his Scientific Legacy***, V. Smentkowski,* General Electric Global Research Center*; **John Russell,*** US Naval Research Laboratory

Introductory remarks about Prof. John T Yates Jr. and his scientific legacy

2:40pm **SS+AS-ThA2 JOHN T. YATES, JR. - The Energizer Bunny (Invited Talk)*, J. William Gadzuk,*** NIST

My friend and colleague John Yates was a joy to share life with. His perpetual enthusiasm, imagination, and sincere interest in whatever happened to be the topic of the moment whether a complex issue in surface science, the fate of an astronomically distant galaxy, the program for Lorin Maazel's next Pittsburgh Symphony concert, the well-being of his scientific "children" and real family, or speculation on what's likely to be tonight's specialties on the menu of our favorite Il Pizzico Restaurant near NIST, was infectious. John's retirement in 2006 from his chair at the University of Pittsburgh [which he went to from NBS/NIST in 1982] brought him to an emeritus-like guest faculty desk at the University of Virginia. Soon upon settling in at the university, his "desk" became an office became a full-fledged surface science lab with an active group of students and post docs supported by research grants that totaled among the highest within UVA chemistry, all of which was built up from scratch after John "retired". He was the only person I know who confessed that he really liked writing research proposals. He lived and executed his retirement with more excitement, energy, and enthusiasm than a young, tenure-seeking assistant professor; the energizer bunny personified.

I will present a number of anecdotal/amusing illustrative vignettes drawn from my experiences with "the energizer bunny" and discuss why his seminal JCP papers on thermal broadening in ESD [**51**,1264(1969)] and on resonance ESD [**90**,5793(1989)] were so influential in my own conceptualization and realizations in surface dynamics.

---

[*] **National Student Award Finalist**

Finally, John and I had the privilege of being co-participants in two NIST Oral History interviews in 2014 and 15, once as a "target" and then as an interviewer [of each other]. This was a great way for us to summarize our nearly half a century of being a part of each other's life, a privilege that I feel very fortunate and honored to have had. [transcripts available upon request: gadzuk@nist.gov [mailto:gadzuk@nist.gov]]

3:00pm **SS+AS-ThA3 Polymer Precursors Studied by Mass Spectrometry, Ion Mobility and Computational Strategies (Invited Talk)**, ***David M. Hercules,*** Vanderbilt University

There has been considerable interest recently in using mass spectrometry and related methods to address structures of complex systems, including block copolymers. Polyurethanes (PURs) are polymers that contain multiple "hard" and "soft" blocks that have different sequences of the same units along the chain. The ultimate goal in studying such materials would be the ability to determine the exact sequence along the chain and to correlate specific sequences with polymer performance. We have established a protocol on smaller molecules that can address this type of issue using the combination mass spectrometry, collision-induced dissociation, ion mobility spectrometry (IMS), and molecular dynamics simulations. A key component of the of the project is the synthesis of model PUR oligomers having authentic component sequences. The individual components are methylene diphenyl diisocyanate (MDI), bis-diol terminated polybutylene adipate (PBA), and 1,4-butane diol (BD), each containing 3 MDIs, 4 PBAs and 4 BDs (MW = 1910). The main collision-induced dissociation fragmentation reactions occur between the PUR and PBA carbonyl groups and BD hydrogen atoms. Additionally, a 1,3 H-shift reaction occurs between the PUR N-H group and BD oxygen. Different fragment ions are observed depending on the unit size and the sequences of the units in the chain. An important aspect of the research is to use IMS to separate compounds that have identical masses but different molecular-ion scattering cross sections. Computational strategies are important for calculation of IMS collisional scattering cross sections and to aid in the interpretation of fragmentation mechanisms. They help to identify synthetic targets that will show the largest effects of the experimental measurements.

3:20pm **SS+AS-ThA4 From Symmetry to Applications: One of Many Journeys Touched by John Yates (Invited Talk)**, ***Ellen Williams,*** Advanced Research Projects Agency - Energy

In the 1970's John Yates spent a sabbatical year at Caltech, where he touched the lives of many students and postdocs working in the group of Prof. Henry Weinberg. My story starts as a young student, fascinated with symmetry and statistical mechanics, who was privileged to work in the laboratory with John, in those early days of surface science when it seemed that every observation opened new horizons.

I will provide highlights of some of the exciting research that followed from those early days of surface science, discussing the impact of scanning tunneling microscopy, the linkages of surface science and nano-electronics, and the practical impacts of many years of fundamental studies from the perspectives of industry and ARPA-E.

4:00pm **SS+AS-ThA6 A Tribute to John T. Yates Jr. and His Pioneering Work with Graphitic Surfaces (Invited Talk)**, ***Patricia A. Thiel,*** Ames Laboratory

John T. Yates, Jr. directed pioneering work on graphitic surfaces. In one case, he and his group prepared graphene on SiC surfaces long before graphene was popularized. In another case, they developed a method to induce surface intercalation of Cs at a graphite surface. In this talk, I will review his contributions and describe the ways in which his work has inspired some of my own. For instance, we have studied adsorption, nucleation, growth, and reaction of dysprosium (Dy) on the basal plane of graphite, and the way that these phenomena are influenced by surface defects. Dysprosium islands nucleate homogeneously on terraces at room temperature. With increasing temperature the shape changes, with islands becoming taller and more facetted. At still higher temperature, Dy reactions with graphite to form carbide. Using the technique developed by John and his group, we can also induce surface intercalation at elevated temperature. We show that this surface intercalation differs significantly from bulk intercalation.

4:20pm **SS+AS-ThA7 Surface Science influenced by Dopants (Invited Talk)**, ***Hajo Freund,*** Fritz Haber Institute of the Max Planck Society, Germany

Model systems are useful to establish structure/morphology reactivity relations in heterogeneous catalysis. Here we use a Metal-Insulator-Metal (MIM) structure to advice CO_2.

We had shown before that ultra-thin oxide films could be used as effective barriers to charge Au islands with electrons from the metal below the support. The idea is to use the electrons stored in the islands to activate molecules by electron transfer. Such a molecule is the energy economy relevant carbon-dioxide for example. We demonstrate adsorption of CO_2 at gold islands and the reversible formation of CO_2 anions and oxalates based on information from microscopy and spectroscopy.

We show how to transfer those ideas developed for thin film systems to bulk materials, where we use appropriate dopants within the support material to provide the electron source. The electron transfer to Au islands as well as the activation of oxygen will be demonstrated.

4:40pm **SS+AS-ThA8 Desorption: Out of the Vacuum, into the Liquid (Invited Talk)**, ***Michael Grunze,*** KIT, Germany; *H.J. Kreuzer,* Dalhousie University, Canada

The first paper on thermal desorption John Yates published with Ted Madey was entitled: *Nitrogen Desorbs with Complex Kinetics*. Thermal Desorption Spectroscopy, in more and more sophisticated experimental set-ups including flow reactors, became then a prominent techniques in John´s Laboratory to study simple and complex surface chemical reactions. In this short report, we look further into "complex kinetics" and find that the theoretical framework of a thermally activated process can not be applied to the detachment of particles in a micro-fluidic shear-flow experiment.

The theoretical description of the desorption process treats bond breaking as a thermally activated process, which can be described by the Arrhenius equation. The activation energy and the pre-exponential factor can be determined from a series of TPD experiments with either varying coverage or at constant coverage, using different heating rates. Here we experimentally and theoretically analyze the detachment of microscopic polystyrene beads from different self-assembled monolayer (SAM) surfaces in a shear flow to develop a mechanistic model for the removal of cells from surfaces. The detachment of the beads from the surface is treated, as in thermal desorption experiments, as a thermally activated process to determine activation barrier and attempt frequency of the rate determing step in bead removal. The statistical analysis of the experimental shear detachment data, obtained in phosphate-buffered saline solution, results in an activation energy of detachment around 20 kJ/mol. This value is orders of magnitude lower than the adhesion energy measured by atomic force microscopy (AFM). The same order of magnitude for the adhesion energy measured by AFM is derived from ab initio calculations of the van der Waals interaction energy between the polystyrene beads and the SAM-covered gold surface. We hence conclude, that the rate determing step for detachment of the beads is the initiation of rolling on the surface (overcoming static friction), and not physical detachment as would be the case in a gas desorption experiment.

5:00pm **SS+AS-ThA9 Infrared Spectroscopy in Surface Science: The Legacy of John T. Yates, Jr. (Invited Talk)**, ***Michael Trenary,*** University of Illinois at Chicago

A constant theme throughout the long scientific career of John T. Yates, Jr. was the use of infrared spectroscopy to probe the properties of surfaces and of adsorbed molecules. In his very first publication in 1961, based on his PhD thesis from MIT, he used transmission infrared spectroscopy to study the interaction of carbon monoxide with alumina-supported nickel surfaces. He continued to use innovative methods of transmission infrared spectroscopy in his laboratories at the National Bureau of Standards, the University of Pittsburgh, and the University of Virginia. The final publication of his career, which appeared in 2016, featured transmission IR spectra of CO interacting with the surfaces of titania-supported gold. In addition to transmission IR spectroscopy of high-area powdered samples, he was also a leader in the use of reflection absorption infrared spectroscopy (RAIRS), also known as infrared reflection absorption spectroscopy (IRAS), a method that allows IR spectra to be obtained on small-area metal single crystals. RAIRS is one of the few surface science techniques that can be used both under UHV conditions as well as in the presence of an ambient pressure of gas. John Yates was a pioneer in bridging the so-called pressure gap by using RAIRS to probe gas-surface interactions in the presence of elevated gas pressures. Recent examples from other research groups will be presented to highlight the continuing impact John Yates has had in the use of infrared spectroscopy in surface science.

5:20pm **SS+AS-ThA10 From Surface Science to New Catalysts (Invited Talk)***, Ib Chorkendorff,* Technical University of Denmark

In this presentation I will give a brief overview of how my post-doc with John T. Yates Jr. influenced my way of working and how that philosophy could be used too go from fundamental investigations of reactions on surfaces to actually understand and make new heterogeneous catalysts. First we shall discuss how mass-selected nanoparticles of CuZn alloys 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 very 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].

References

1. S. Kuld, C. Conradsen, P.G. Moses, I. Chorkendorff and J. Sehested, Angew. Chemie 53 (2014) 1.

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

3. S. Kuld, M. Thorhauge, H. Falsig, C. Elkjær, S. Helveg, I. Chorkendorff, J. Sehested, Accepted SCIENCE (2016).

4. F. Studt, F. Abild-Pedersen, I. Sharafutdinov, C. F. Elkær, J. S. Hummelshøj, S. Dahl, I. Chorkendorff, and J. K. Nørskov, Nature Chemistry. 6 (2014) 320.

5. J. Greeley, I.E.L. Stephens, A.S. Bondarenko, T. P. Johansson, H. A. Hansen, T. F. Jaramillo, J. Rossmeisl, I. Chorkendorff, J. K. Nørskov, , Nature Chem. 1 (2009) 522.

6. M. Escudero-Escribano, P. Malacrida, M- Hansen, U. G. Vej-Hansen, A. Velázquez-Palenzuela V. Tripkovic, J. Schøitz, J. Rossmeisl, I. E.L. Stephens, I. Chorkendorff, SCIENCE 352 (2016) 73-76.

7. P. Hernandez-Fernandez, F. Masini, D. N. McCarthy, C. E. Strebel, D. Friebel, D. Deiana, P. Malacrida, A. Nierhoff, A. Bodin, A. M. Wise, J. H. Nielsen, T. W. Hansen, A. Nilsson, I. E.L. Stephens, I. Chorkendorff, Nature Chemistry 6 (2014) 732-8.

8. A. Velázquez-Palenzuela, F. Masini, A. F. Pedersen, M. Escudero-Escribano, D. Deiana, P. Malacrida, T. W. Hansen, D. Friebel, A. Nilsson, I. E.L. Stephens, I. Chorkendorff, J. Catal. 328 (2015) 297-307.

5:40pm **SS+AS-ThA11 Activation of Carbon Dioxide on Metal and Carbide Surfaces (Invited Talk)***, Jingguang Chen,* Columbia University

Converting CO_2 into valuable chemicals and fuels is one of the most practical routes for reducing CO_2 emissions while fossil fuels continue to dominate the energy sector. The catalytic reduction of CO_2 by H_2 can lead to the formation of three types of products: CO through the reverse water-gas shift (RWGS) reaction [1], methanol via selective hydrogenation [2], and hydrocarbons through combination of CO_2 reduction with Fischer-Tropsch (FT) reactions. In the current talk we will discuss some of our recent results in CO_2 conversion [3]. Our research approaches involve the combination of DFT calculations and surface science studies over single crystal surfaces, catalytic evaluations over supported catalysts, and in-situ characterization under reaction conditions. We will also discuss challenges and opportunities in this important research field [4].

References:

[1] M.D. Porosoff, X. Yang, J.A. Boscoboinik, and J.G. Chen, “Molybdenum carbide as alternative catalysts to precious metals for highly selective reduction of CO_2 to CO”, *Angewandte Chemie International Edition*, 53 (2014) 6705-6709.

[2] X. Yang, S. Kattel, S.D. Senanayake, J.A. Boscoboinik, X. Nie, J. Graciani, J.A. Rodriguez, P. Liu, D.J. Stacchiola and J.G. Chen, “Low pressure CO_2 hydrogenation to methanol over gold nanoparticles activated on a $CeOx/TiO_2$ interface”,*Journal of the American Chemical Society*, 137 (2015) 10104-10107.

[3] M.D. Porosoff, M. Myint, S. Kattel, Z. Xie, E. Gomez, P. Liu and J.G. Chen, “Identifying different types of catalysts for CO_2 reduction by ethane through dry reforming and oxidative dehydrogenation”, *Angewandte Chemie International Edition*, 54 (2015) 15501-15505.

[4] M.D. Porosoff, B. Yan and J.G. Chen, “Catalytic reduction of CO_2 by H_2 for synthesis of CO, methanol and hydrocarbons: Challenges and opportunities”, *Energy & Environmental Science*, 9 (2016) 62-73.

6:00pm **SS+AS-ThA12 Thermodynamic Control of TTF-TCNQ Molecular Layers on Metallic Surfaces (Invited Talk)***, Petro Maksymovych,* Oak Ridge National Laboratory

Bulk molecular ionic solids exhibit a fascinating diversity of electronic ground states, including unconventional superconductivity. The electronic properties of these systems have historically avoided surface analytical studies due to the intrinsic difficulty with surface preparation. We are therefore pursuing epitaxial growth of charge-transfer compounds, toward understanding their fundamental properties and creating new kinds of metal-organic or organic-organic interfaces [1,2]. A primary challenge is to assure compatibility of supported epilayers with the redox processes so as to enable, enhance but not eliminate significant charge transfer and electron correlations with supported structures.

In this talk, I will discuss 2D molecular structures of TTF and TCNQ molecules supported on metal and graphitic surfaces. We established that these molecules self-organize into a "zoo" well-ordered structure with a wide-range of TTF:TCNQ ratios [3] - a marked deviation from a single stable 1:1 ratio in the bulk. We propose that the formation these structures is governed by a surface phase diagram that exhibits at least four distinct stable compositions. The diagrammatic picture explains many of the properties of such systems that often seem incidental: the morphology of epilayers, governed by nucleation and growth; coexistence and abundance of various phases, and the distinct molecular structure of phase boundaries. Using coupled image and computational analysis, we conclude that the observed shapes are dictated by the preferential formation of a well-defined “quad”-motif involving TTF(TCNQ) molecules coordinated by at least four of its matching neighbors. Thus enabled deterministic control is beneficial to both electronic properties of surface phases (which can develop local magnetic moments) and the formation of quasi-2D TTF-TCNQ solids, which develop decidedly non-bulk Mott-insulating state despite having 1:1 bulk ratio. We anticipate that these properties are quite general for multicomponent molecular compounds, providing new opportunities for self-organized and electronically interesting molecular systems.

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

[1] G. A. Rojas et. al, and P. Maksymovych, "Ionic Disproportionation of Charge Transfer Salt Driven by Surface Epitaxy", J. Phys. Chem. C, 117 (2013) 19402.

[2] C. Park et. al, and P. Maksymovych, "Weak competing interactions control assembly of strongly bonded TCNQ ionic acceptor molecules on silver surfaces", Phys. Rev. B 90 (2014) 125432.

[3] S. Jeon et. al and P. Maksymovych, ACS Nano in review (2016).

Surface Science
Room 104E - Session SS+HC-FrM
Deposition and Analysis of Complex Interfaces

Moderators: Bruce D. Kay, Pacific Northwest National Laboratory, Daniel Killelea, Loyola University Chicago

8:20am **SS+HC-FrM1 A Quantitative, Experimentally Supported Model for Surface Energy (SE) as a Function of Surface Defect Density (DD): the SEDD Model - Comparison with Three Liquid Contact Angle Analysis and AFM***, **Abijith Krishnan**,* Arizona State University/BASIS HS Scottsdale/SiO2 Innovates LLC*; N.X. Herbots,* Arizona State University/SiO2 Innovates LLC*; Y.W. Pershad,* Arizona State University/BASIS HS Scottsdale/SiO2 Innovates LLC*; S.D. Whaley,* SiO2 Innovates LLC/Arizona State University*; R.J. Culbertson, R.B. Bennett-Kennett,* Arizona State University

Metal Oxide Semiconductor Field Emission Transistors (MOSFETs) have been key to micro- and nano-electronics for the past six decades, but electrically active defects resulting from dangling bonds (unbounded electrons) or mobile ions create parasitic charges, known as surface charges (Q_{ss} for dangling bonds and Q_o for mobile ions), that limit performance. Passivation via oxygen and hydrogen species can reduce surface defects. However, surface state charge analysis via capacitance-voltage (C-V) curves is used to evaluate the extent of passivation but does not accurately reflect the number of structural defects. On the other hand, surface characterization by Tapping Mode Atomic Force Microscopy (TMAFM) can be used for topographic observation and surface roughness measurements but has not been used to measure surface defect density. The new theoretical model proposed the Surface Energy Defect Density (SEDD) Model [1] aims to relate surface defect density to surface energy, a macroscopic quantity measured via high statistics Three Liquid Contact Angle Analysis (3LCAA) metrology [2,3]. Three Liquid Contact Angle Analysis (3LCAA) conducted in a class 100 clean-room using the Sessile Drop method and the Van Oss theory enables for accurate and reproducible contacts angles analysis within 1°, and a reproducible relative error lower than 2-3% for the total surface energy. These results have led to the conception a new theoretical model, the Surface Energy -Defect Density Model (SEDD) which relates the macroscopic surface energy density to the microscopic defect density. To test this model with experimental defect densities, this work uses PIXNANOVERT, a new algorithm to extract defect densities from high resolution large area (1 x10 μm^2) TMAFM topographs taken on Si(100) passivated by the Herbots-Atluri process [5-7]. Analysis using surface effect density extracted. PIXNANOVERT shows that the SEDD Model predicts, within 5 the measured surface defect densities of oxidized Si surfaces with known surface energies. With this model, MOSFET manufacturers can determine the defect density in the oxide interface of their transistors by measuring the surface energy of the oxide. Testing transistor effectiveness for computers and other electronic devices would thus become more accurate than relying on C-V curves to quantify surface charge density. The SEDD Model would also allow us to determine the surface chemistry (e.g. hydrophobicity) of many other crystalline or amorphous materials, such as polymers and glasses, by measuring the surface energy.

[1] AS Krishnan, Senior Thesis (2016)

[2] Pat. pend., Herbots et al. (2011,2012,2016)

[3] SD Whaley, PhD, ASU (2013)

8:40am **SS+HC-FrM2 Ab initio Analysis of Elementary Reactions during ALD Tungsten Nucleation on Selective Substrates***, **Mariah King**, G.N. Parsons,* North Carolina State University

In 1987, selective deposition of tungsten via silane reduction was confirmed with a high deposition rate at a low temperature. Despite the numerous studies that have been conducted in the following years, many chemical processes that control selective tungsten ALD growth are not yet sufficiently understood and the leading concern remains that, past the “selective window”, uniform deposition is observed on silica, the non-reactive surface. This loss of selectivity is due to the ability of the non-selective surface to promote nucleation in time due to surface processes and chemical reactions. The primary cause of tungsten nucleation on silica is a long-standing problem in the semiconductor industry that will require new fundamental understanding and an accurate description of the reaction kinetics between reactants and substrates at the atomic level**.** In this computational study, we use density functional theory to study the reaction energetics, structural stability, and electronic distribution to describe initial reactions during ALD tungsten nucleation on silicon, silica and tungsten substrates. The objective is to identify reactions that have a lower probability of occurrence, but may lead to defects that enable nucleation on otherwise non-reactive surfaces. Understanding the probability at which a species reacts with a pristine non-reactive surface will enable designers to define the limits of process defect generation, thereby identifying viable process options. Additionally, these simulations are used to suggest alternative system conditions that could lead to improved selectivity.

As a first step towards understanding the kinetics of complex deposition reactions, we present the kinetics of the elementary reactions for silane and tungsten deposition on silica and fluorinated tungsten surfaces. Along with intensive experimental data on this specific system, we have used the calculated reaction energetics to suggest the most probable series of reactions that lead to loss of selectivity. Extending these results will allow us to define viable options and directions for highly selective processes that minimize defect creation and propagation in electronic device manufacturing.

9:00am **SS+HC-FrM3 Design and Synthesis of Nanofence Cerium Oxide Coated Platinum Catalysts via Facet-selective Atomic Layer Deposition***, **Kun Cao**, J.M. Cai,* State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology, China*; R. Chen,* State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, School of Optical and Electronic Information, Huazhong University of Science and Technology, China

Sintering of Pt nanoparticles (NPs) catalysts at elevated working temperature is highly undesirable, as coalescence of NPs will cause significant decrease in the number of active sites and resulting catalytic performance degradation. Oxide overcoating techniques have been recently developed to minimize Pt sintering. However, certain trade-off has to be made between stabilization and reactivity. Stabilize metal nanoparticles and simultaneously enhance catalytic activity is still very challenging.

Here, we designed a cerium oxide nanofence coating structure to stabilize Pt NPs using facet selective atomic layer deposition. The facet selectivity is realized through differences in binding energy of Ce precursor fragments Pt surfaces. CeO_x prefers to selectively deposit on Pt (111) facets, while leaving the Pt (100) surface intact. CeO_x has synergy with metal as coating layer and creates highly active sites at Pt-CeOx interfaces. From stability point of view, CeO_x anchors Pt NPs with a strong metal oxide interaction, and nanofence coating layer provide physical blocking that suppresses NP particle migration. Such nanofence CeO_x coated Pt catalysts show both enhanced CO conversion activity and improved sintering resistance up to 700 °C under oxidative atmospheric condition.

9:20am **SS+HC-FrM4 Dehydrogenation and Rehybridization of ZnTPP on Ag(100) and Ag(111)***, C. Ruggieri, S. Rangan, **Robert Bartynski**,* Rutgers, the State University of New Jersey*; E. Galoppini,* Rutgers - Newark

The interactions between zinc(II) tetraphenylporphyrin (ZnTPP) molecules and the Ag(100) and Ag(111) surfaces were investigated using a combination of scanning tunneling microscopy as a local probe of the molecular adsorption configuration and X-ray, ultraviolet, and inverse photoemission spectroscopies as probes of the electronic structure. When forming a molecular monolayer by desorption of a multilayer on the Ag(100) surface, an order molecular array in registry with the substrate and having a square unit cell results. A similar preparation on the Ag(111) surface produces an overlayer that is considerably less dense but is also commensurate with the substrate having a unit cell that is slightly rectangular. Subsequent annealing leads to a transition from intact molecular adsorption to dehydrogenation and subsequent intramolecular and intermolecular rehybridization. Upon annealing, the molecule flattens as the phenyl portions of the molecule form bonds with a neighboring pyrrole group. This leads to a measurable alteration of the electronic structure. In addition, we find evidence of bonding between neighboring rehybridized molecules, consistent with the formation of biphenylene-type structures, leading to the growth of extended two-dimensional covalently bound structures. Understanding basic rules for molecule-molecule hybridization, potentially templated by prior self-assembly, could enable the directed formation of large, complex, and ordered 2-dimensional arrays of organic or metalorganic units.

C. Ruggieri, S. Rangan, R.A. Bartynski, and E. Galoppini, J. Phys. Chem. C 120, 7575 (2016)

9:40am **SS+HC-FrM5 A Case Study of the SMSI Effects: CO Oxidation on the TiO_x/Pt(111) Model Surfaces***, **Mingshu Chen**, H. Li, X.F. Weng, H. Zhang, H.L. Wan,* Xiamen University, China

Well-ordered ultrathin TiO_x films were grown on Pt(111) as model surfaces to probe the effects of the strong metal-support interaction (SMSI) on the catalytic performance. The model surfaces of TiO_x/Pt(111) were prepared under UHV and characterized by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). CO oxidation was tested for the model surfaces in a batch reaction cell as a function of the TiO_x coverages and structures. And a home-built reflection adsorption infrared spectroscopy (IRAS) was used for *in-situ* studying the surface species and stability of the model surfaces under the reaction conditions. The results show that catalytic activity could be improved significantly on the monolayer z-TiO_x, while a maximum is achieved at 0.3~0.5 ML for the w-TiO_x. The TiO_x thin films were found to be stable under CO oxidation conditions. The activation energy for CO oxidation reaction on the 1 ML z-TiO_x/Pt(111) was found to be 46 kJ/mol, which is much lower than that of 87 kJ/mol on the clean Pt(111) surface.

10:00am **SS+HC-FrM6 Toluene and Benzyl Radical Formation during Deoxygenation of Phenylmethanol on Rutile TiO_2(110)***, **Long Chen**, R.S. Smith, B.D. Kay, Z. Dohnalek,* Pacific Northwest National Laboratory

Understanding the reaction pathways of lignin-derived molecules on catalyst surfaces is of great importance for the sustainable production of energy carriers. In this regard, the role of radicals in the reaction mechanisms leading to functionalized aromatics has been extensively argued. The involvement of radical species has been firmly established for a number of simpler reactions on high surface area oxide catalysts, such as oxidative coupling of methane and selective oxidation of propylene. However, the formation of free radicals is rarely demonstrated. In this work, the reaction pathways of simple lignin-derived aromatic alcohols, i.e. phenol, phenylmethanol, and 2-phenylethanol, on a prototypical model oxide surface, rutile TiO_2(110), are studied using a combination of molecular beam dosing and temperature programmed desorption (TPD). For phenylmethanol, the coverage dependent TPD data show that about 40% of molecules adsorbed on the surface at a saturation coverage are converted to reaction products indicating that the reactions proceed on regular five-fold coordinated Ti sites. This is in contrast to aliphatic alcohols where the reactions are shown to proceed exclusively on bridging oxygen vacancy defect sites. The studies of OD-labelled phenylmethanol demonstrate that a fraction of OD hydrogen is transferred to the benzyl group to form toluene that desorbs between 300 K and 480 K. In the competing reaction, the OD hydrogen is converted to water at ~350 K. Once the OD hydrogen is depleted above 480 K, the remaining plenylmethoxy surface species dissociate yielding benzyl radicals in the gas phase. Combined, these results show that the conversion of phenylmethanol on TiO_2(110) proceeds via a unique chemistry. In contrast, both phenol and 2-phenylethanol exhibit expected surface chemistry analogous to that of aliphatic alcohols. These findings reveal for the first time the formation of free radical species from the interaction of phenylmethanol with TiO_2(110) and demonstrate a new direct mechanism for deoxygenation of lignin-derived benzylic alcohols to aromatics on TiO_2.

Author Index

Bold page numbers indicate presenter

Author Index

Author Index

Author Index

Author Index