Sunday Afternoon, October 21, 2018

Biomaterials Plenary Session
Room 101B - Session BP-SuA

AVS BIP & AIP IPF Forum Plenary Session

Moderator: Joe Baio, Oregon State University

3:00pm **BP-SuA1 Integrating Single Molecule Devices with Conventional Microfabrication using DNA Origami***, Paul Rothemund,* California Institute of Technology **INVITED**

For several decades nanotechnology has promised a variety of extraordinary advances, from medical nanorobots to molecule-scale electronics. The basic idea behind this promise is that individual molecules, or precise arrangements of molecules, will have new computational or functional properties that are impossible to achieve by shaping materials with conventional fabrication techniques. Yet despite breakthroughs in our ability to organize molecules into complex devices through the use of self-assembling DNA scaffolds, we are still far from a mature nanotechnology which can deliver on these promises. The question is, what stands in our way? One answer is that it is still very difficult to organize thousands of molecular devices into larger more complex architectures, to get information and instructions into them, and to get results out of them. This talk will examine how to combine conventional silicon microfabrication with the DNA origami method for making molecular shapes. In particular, we will show that our ability to program the shape of large DNA structures enables the use of lithography to write large-scale patterns of single molecule binding sites. Then the DNA shapes can act as adaptors, slotting molecular devices into micron scale microfabricated devices with yields that are far greater than those achieved by typical Poisson-limited assembly processes. Design of the binding energy landscape enables symmetry-breaking and precise orientation of the shapes. Finally, we demonstrate the technique by positioning and orienting tens of thousands of molecular light emitters within photonic crystal cavities, controlling both the intensity and polarization of emission. Potential application of the technique for the highly multiplexed detection of disease biomarkers will be discussed.

3:40pm **BP-SuA3 High Resolution Cryo-EM Structures of Macromolecular Complexes***, Wah Chiu,* Stanford University **INVITED**

The advances of cryo-EM have made it possible to determine atomic resolution structures of biochemically purified macromolecular complexes equivalent to those solved by X-ray crystallography. Validation procedure has been implemented to assess the structure accuracy and reliability. We will present biological examples that can be derived from this imaging approach in terms of their functional mechanisms.

2D Materials Focus Topic
Room 201B - Session 2D+EM+MI+NS+TF-MoM

2D Materials Growth and Fabrication

Moderator: Jing Xia, University of California Irvine

8:20am **2D+EM+MI+NS+TF-MoM1 Wafer Scale Epitaxial Growth of Monolayer and Few-Layer WS_2 by Gas Source Chemical Vapor Deposition***, **Mikhail Chubarov**, T.H. Choudhury, J.M. Redwing,* The Pennsylvania State University

Tungsten disulfide (WS_2) has been widely investigated due to its outstanding properties compared to other 2D TMD including a bandgap of 2 eV, relatively high theoretical electron mobility, valley spin polarization, among others. Commonly, the films are grown on amorphous substrates like SiO_2 and, consequently, consist of high angle grain boundaries after coalescence due to the random orientation of domains. These can act as scattering and recombination centers for charge carriers limiting device performance. To avoid this, a crystalline substrate and epitaxial growth is typically employed for general thin film deposition although this approach has not been extensively investigated for 2D TMD monolayers. Large area growth is also crucial to show technological feasibility of the material for wafer-scale device fabrication.

In this work, we employ cold wall gas source chemical vapor deposition for the growth of WS_2 films on 2” (0001) α-Al_2O_3. To achieve coalesced monolayer growth over the entire substrate, we implemented a multi-step growth process modulating the metal precursor concentration during each of the steps. $W(CO)_6$ and H_2S were used as precursors in H_2 carrier gas. The deposition experiments were conducted over the temperature range from 750 °C to 1000 °C at a pressure of 50 Torr. Characterization of resulting samples was conducted using atomic force microscopy (AFM), in-plane X-ray diffraction (XRD) and room temperature Raman and photoluminescence (PL) measurements.

Initial studies showed that the WS_2 films exhibit multiple crystal orientations which evolve with growth temperature. At lower deposition temperature (750 °C), two orientations rotated 30° one from another were observed. At the high deposition temperature (1000 °C), five different crystal orientations were present. Among others, orientation with epitaxial relation of (10-10)WS_2//(10-10)α-Al_2O_3 was present at all temperatures. It was established that the unwanted orientations can be suppressed by increasing the H_2S concentration. Further adjustment of the growth and use of the multi-step growth process led to the formation of a coalesced epitaxial monolayer WS_2 on α-Al_2O_3 with XRD FWHM of 10-10 peak in ω being 0.09°. This value suggests well in-plane oriented domains with low edge dislocation density. A high intensity, narrow (FWHM=40 meV) PL peak positioned at 2.01 eV was observed for WS_2 films. Monolayer formation was confirmed from the AFM height profile (D =0.9 nm) and Raman measurements by observing spectral region where layer breathing and shear modes would appear. A fully coalesced, monolayer film was achieved using the multi-step growth process in a total time of 80 minutes.

8:40am **2D+EM+MI+NS+TF-MoM2 Wafer Scale Deposition of Monolayer Transition Metal Dichalcogenides***, **Kortney Almeida**, M. Wurch, G. Stecklein, L. Bartels,* University of California, Riverside

Monolayer transition metal dichalcogenide (TMD) films are promising materials in the continuing development of nanoscale devices. Methods to produce wafer-scale monolayer TMD films have included tube-furnace chemical vapor deposition (CVD), liquid-phase exfoliation, and metal-organic CVD. These methods suffer from issues with particulate contamination, pyrophoric precursors, and high cost. Here we demonstrate the growth of homogeneous wafer-scale monolayer molybdenum disulfide (MoS_2) using solid inorganic and liquid organic precursors in a high-vacuum environment. These results are achieved using an amorphous SiO_2substrate and without any powder or metal-organic precursors. Growth proceeds by the decomposition of carbon disulfide at a hot molybdenum filament, which yields volatile MoS_xprecursors that precipitate onto a heated wafer. The continuous and homogeneous single-layer film of $MoS_2$is deposited at wafer scale with a total growth time of fifty minutes. Various thicknesses of the thin films are also demonstrated by the manipulation of the filament power. Optical and electrical characterization indicates performance comparable to or better than MoS_2film grown by other wafer-scale growth techniques. Our method provides a scalable process to deposit thin TMD films in a high vacuum environment.

9:00am **2D+EM+MI+NS+TF-MoM3 Crystal Growth of 2D Materials: From Model Systems to Integrated Manufacturing***, **Stephan Hofmann**,* University of Cambridge, UK **INVITED**

In order to serve the industrial demand for “electronic-grade” 2D materials, we focus on chemical vapour deposition (CVD), and in this talk I will review our recent progress in scalable CVD [1] and device integration approaches of highly crystalline graphene, hexagonal boron nitride (h-BN) and transition metal dichalcogenide films. The systematic use of in-situ metrology, ranging from high-pressure XPS to environmental electron microscopy, allows us to reveal some of the key growth mechanisms for these 2D materials that dictate crystal phase, micro-structure, defects, and heterogeneous integration control at industrially relevant conditions [2,3]. I will focus on tailored CVD processes to achieve large monolayer h-BN domains with lateral sizes exceeding 0.5 mm. Importantly we show that depending on the process catalyst as-grown h-BN mono-layers can be easily and cleanly transferred using an entirely exfoliation-based approach.[4] We demonstrate sequential h-BN pick-up, opening a pathway to integrate CVD films in high quality 2D material heterostructures. Progress in growth reached a level where adequate characterisation of such 2D crystal layers over large areas has become a key challenge. Hence we also explore new non-contact characterisation methods [5,6]. We work on applications ranging from magentic tunnel junctions [7] to sensing and single molecule analysis [8,9], and the talk will focus on some of the diverse yet connected integration challenges for CVD 2D films that present a key bottleneck towards reliable scale-up manufacturing and commercialisation.

References

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2. Weatherup et al., Nano Lett. 16, 6196 (2016).

3. Caneva et al. Nano Lett. 16, 1250 (2016).

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5. Lin et al., Sci. Rep. 7, 10625 (2017).

6. Feng et al., Nano Lett. 18, 1739 (2018).

7. Piquemal-Banci et al., ACS Nano (2018).

8. Dahmke et al., ACS Nano 11, 11108 (2017).

9. Walker et al., ACS Nano 11, 1340 (2017).

9:40am **2D+EM+MI+NS+TF-MoM5 Understanding the Edge-Controlled Growth and Etching in Two-Dimensional Materials***, **Kai Xiao**, X. Li, X. Sang,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; W. Zhao, J. Dong,* Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan,44919, South Korea*; A. Purektzy,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; C. Rouleau,* Center for Functional Nanomaterials Brookhaven National Laboratory*; F. Ding,* Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan,44919, South Korea*; R.R. Unocic, D.B. Geohegan,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Understanding the atomistic mechanisms governing the growth and etching of two-dimensional (2D) materials is of great importance in guiding the synthesis of large area, single-crystalline, high quality 2D crystals and heterostructures. In this talk, the growth-etching-regrowth process of monolayer 2D crystals by a CVD method will be discussed. We found that switching from growth to etching formed pores with various shapes in the single crystal domains which can be explained by edge-structure dependent growth process. In addition, combined with first principles theory, and ab initio simulations, in situ STEM imaging was used to understand the evolution of edge structure around pores in monolayers as a function of temperature and Mo chemical potential. Our results demonstrate that by varying the local chemical environment, we can trigger formation of 2D monolayer nanostructures terminated by different edge reconstructions during in situ heating and electron beam irradiation and form edge structures with metallic and/or magnetic properties. The ability to synthesize 2D nanostructures with metastable NW edges having predictable atomic structures opens the door to a wide range of novel 2D materials and heterosturctures with electrical and magnetic properties as revealed by DFT, which could potentially act as functional building blocks for next-generation nano-devices.

References:

[1] X. Li, J. Dong, J. C. Idrobo, A. A. Puretzky, C. M. Rouleau, D. B. Geohegan, F. Ding, K. Xiao, J. Am. Chem. Soc. 139, 482 (2017).

[2] X. Sang, X. Li, W. Zhao, J. Dong, C. M. Rouleau, D. B. Geohegan, F. Ding, K. Xiao, R. R. Unocic, Nature Comm. Accepted (2018).

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10:00am **2D+EM+MI+NS+TF-MoM6 Synthesis and Characterization of 1T, 1T', and 2H MoTe$_2$ Thin Films***, **Thomas Empante**,* University of California, Riverside*; Y. Zhou,* Stanford University*; S.A. Naghibi Alvillar,* El Camino College*; E.J. Reed,* Stanford University*; L. Bartels,* University of California, Riverside

Transition metal dichalcogenides (TMDs) have been of interest over the past few decades for their intriguing structural, electronic, and optoelectronic properties, particularly when scaled down to thin films. One of the most interesting TMD materials is molybdenum ditelluride (MoTe$_2$) because of its relative ease to attain multiple phases at room temperature, namely the metallic 1T' phase and the semiconducting 2H phase. Here we show a facile chemical vapor deposition process to synthesis not only the aforementioned phases but the elusive unreconstructed 1T phase by regulating the cooling rate and the addition of carbon dioxide during the reaction. Our experimental Raman spectroscopy results were compared to theoretical density functional theory calculations which verify the synthesis of all three phases. Electronic transport measurements were also used to characterize the films and show that the newly synthesized 1T phase is in good agreement with theoretical models depicting semi-metallicity as the material shows increased conductivity with elevated temperatures. In addition to the pure phase materials, mixed phase materials, such as 2H/1T, can be synthesized with slight alterations to the parameters leading to enhancements of the 2H phases' conductivity.

11:20am **2D+EM+MI+NS+TF-MoM10 Low-Defect, High-Uniformity Transfer-Free Graphene on SiO$_2$ by Thermal Chemical Vapor Deposition***, **Leslie Chan**, D.S. Tsai, Z. Wang, C. Carraro, R. Maboudian,* University of California, Berkeley

Chemical vapor deposition (CVD) has emerged as the customary approach for scalable, controllable production of graphene for integrated devices. Standard CVD graphene must be transferred from a generic metal growth substrate onto the desired substrate (*e.g.*, SiO$_2$), but this extra transfer often leads to wrinkles, contamination, and breakage that ultimately result in poor device performance. Several groups have demonstrated metal-catalyzed direct CVD-graphene growth on insulating substrates, but the final graphene products are deficient in quality and uniformity. This work details an expansion of the parameter space that enables lower-defect, higher-uniformity graphene than previously reported using nickel and copper catalysts, respectively. We introduce a mechanism based on carbon permeability that provides deeper insight into the growth process. Ultimately, these studies seek to inform the judicious choice of process parameters that will lead to large-area, high-quality, layer-controlled graphene directly on target substrates.

Applied Surface Science Division
Room 204 - Session AS-MoM

Quantitative Surface Analysis

Moderators: Kateryna Artyushkova, University of New Mexico, Tim Nunney, Thermo Fisher Scientific, UK

8:20am **AS-MoM1 A Fistful of Data: The Good, the Bad and the Ugly of Quantitative Surface Analysis***, **Alexander Shard**,* National Physical Laboratory, UK **INVITED**

The properties of surfaces and interfaces govern the performance of most manufactured items, from advanced electronic devices, medical devices to packaging materials. The chemical analysis of such surfaces underpins the development of new products with better performance, ensures consistency in production and identifies the causes of failure. Commonly used methods, such as XPS and SIMS, can detect elements and chemical species, but also contain information on the amount of material and its distribution. This talk will describe the application of XPS and SIMS in the measurement of surface chemistry, highlighting the wealth of information available and the areas that need attention and development.

The measurement of coating thickness and the identification of defects is of major importance and will be a focus of attention. For thin (<10 nm) oxide films on silicon, XPS has been shown to be the most accurate method for such measurements and relies on a length scale that must be established by comparison with other methods. The applicability of XPS to other materials, non-planar samples and thicker films has improved in recent years and these developments will be described along with the potential use of both the inelastic background shape and HAXPES to extend the information depth, in some cases to more than 100 nm. The use of SIMS to measure surface composition is a particular priority, particularly in organic materials. Recent descriptions of matrix effects have highlighted the potential magnitude of this problem, but also point to methods to mitigate it. Although matrix effects are often taken into account when attempting to perform quantitative chemical analysis, their effects in SIMS images and depth profiles are often ignored but can be of overwhelming importance.

Recent international inter-laboratory studies have demonstrated that there can be significant disparity in the quantitative results reported by laboratories analysing the same materials using these techniques. The major causes of this variability will be discussed and shown to be predominantly due to the use, or misuse, of interpretational algorithms and reference data. The talk will highlight the role of ISO TC201 and VAMAS TWA2 in improving comparability and reproducibility in the results of these analytical methods.

9:00am **AS-MoM3 XPS and the Reproducibility Crisis***, **Donald Baer**, M.H. Engelhard,* Pacific Northwest National Laboratory

There is a growing awareness of reproducibility issues in many areas of science, including those associated with the AVS. In a 2016 survey of 1576 scientists reported in Nature (533 (2016) 452-454), 90% of those interviewed indicated that there was at least some level of reproducibility crisis in the scientific literature and more than half indicated that the crisis was significant. Data reproducibility and replication issues appear to be systemic and occur at multiple levels in the scientific process (in addition to fraud which is real but infrequent and not the focus here) including: i) within in a single study (Are results within one study appropriately reproducible, internally consistent, and adequately reported?), ii) within a laboratory (Have research groups established clear procedures and protocols to pass on to others the details needed for reproducing materials or other aspects of research?), iii) in reported results (Are measurement approaches and information in publications adequately detailed so that others could reproduce the work?). As the most commonly applied surface analysis method, use (or misuse) of XPS is a contributor to reproducibility issues but XPS is also an important tool that can be used to address some of the problems. Because of the high importance of the surface composition and chemistry on behaviors of materials as well as in biological and environmental systems, the use of XPS has been increasing for at least two decades. In the area of nanoparticles, lack of surface characterization is one source of material non-reproducibility. However, many researchers lack the experience or expertise needed to obtain the information sought from XPS measurements in useful and reproducible ways. Multiple types of problems appear and many of them can be observed in the literature including: analysis of samples at an inappropriate times or in non-optimal conditions; inappropriate handling and preparation of samples; damage to samples during analysis leading to faulty conclusions; incorrect or inconsistent quantification and/or spectral interpretation; lack of calibration and/or incorrect instrument set up; chemically meaningless fitting of data; inadequate reporting of methods, processes and results. This talk highlights examples of where XPS has been a tool for addressing reproducibility challenges, show a few examples of problem areas and summarize actions that the AVS is undertaking to help address reproducibility issues.

9:20am **AS-MoM4 Rapid Calculation Method of the Voigt Function for Use in the Analysis of Photoelectron Spectroscopic Data***, **Peter Sherwood**,* University of Washington

The basic shape of a photoelectron peak is Lorentzian, which is modified by instrumental and other factors, such as phonon broadening, to give a Gaussian contribution resulting in a peak shape that is a convolution of a Gaussian and a Lorentzian peak shape. The use of the correct peak shape is important in the analysis of photoelectron spectroscopic data. X-ray photoelectron spectra (XPS) from the core region often contain overlapping peaks which can be analyzed by fitting the experimental spectrum to a spectrum generated by the sum of a series of functions, each of which represent the individual peaks together with a background function.[1] XPS from the valence band region can be interpreted by calculating a spectrum from an appropriate model for the solid under study such as a band structure calculation, an approach which requires the inclusion of the photoelectron peak shape in order to correctly model the experimental spectrum.[2]

The Voigt function is a convolution of a Gaussian and Lorentzian and is the best representation for photoelectron peaks. Unfortunately the Voigt function cannot be represented directly as an analytical function and has to be evaluated numerically. Analytical functions were developed to approximate the Voigt function, and a number of so-called pseudo-Voigt functions have been developed. Analytical functions and their partial differentials can be calculated rapidly. One of the early pseudo-Voigt functions was a product function published by the author in 1979.[3]

The presentation will focus on how the true Voigt function can be rapidly calculated at speeds that are comparable to the calculation of pseudo-Voigt functions, with CPU times of a fraction of a second for complex curve fitting calculations on computers using Intel Core i7 processors.[4] The approach is based on the extensive work on the Voigt function by the atmospheric sciences community. Examples will be provided showing the application of the true Voigt function to the curve fitting of experimental core XPS data and the modelling of experimental valence band XPS data.

Reference

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3. R.O.Ansell,T.Dickinson,A.F.Povey,and P.M.A.Sherwood, *J. Electroanal. Chem.* **1979,** *98*, 79.

4. P.M.A. Sherwood, *submitted for publication.*

9:40am **AS-MoM5 Statistical Analysis and Peak Fitting of X-ray Photoelectron Spectroscopy Data. Good Practices and Procedures for Working up this Information.*, Matthew Richard Linford,*** *V. Jain,* Brigham Young University

Determining appropriate methods of peak fitting X-ray photoelectron spectroscopy (XPS) data remains an active area of research. In this talk we discuss some of our recent efforts to better understand and interpret XPS narrow and survey scans. These include a description and comparison of the Gaussian-Lorentzian sum (GLS) and product (GLP) functions and their use in XPS peak fitting. This discussion will include a description of the shapes of the GLS and GLP as a function of the mixing parameter in their definitions and a comparison of these functions to the Voigt function. We will also discuss uniqueness plots as used to identify fit parameter correlation, width functions for identifying changes in peak envelopes, and principal components analysis, multivariate curve resolution, and pattern recognition entropy for studying and comparing series/groups of spectra. Finally, we also hope to briefly mention the importance of other statistical tools for better understanding XPS peak fitting. These include using chi squared to compare fits, showing the residuals to identify poor fits and/or questionable parts of fits, showing the sum of the fit components as a comparison to the original spectra, and employing the Abbe criterion for identifying correlated residuals.

10:00am **AS-MoM6 Modeling the Shirley Background*, Alberto Herrera-Gomez,*** *D. Mulato-Gomez,* Cinvestav-Unidad Queretaro, Mexico*; A.D. Dutoi,* University of the Pacific

In quantitative chemical studies employing X-ray photoelectron spectroscopy, the total background signal can be well described as the sum of two terms, one originated from inelastic electron-energy losses and another that is expounded by the empirical Shirley method [1,2]. The inelastic part is very well quantified by the Tougaard theory proposed in 1982 [3]; the Shirley part, in the near-peak region, can be quantified by the method illustrated by Proctor and Sherwood [4]. Since the Tougaard background meets the experimental signal at binding energies ~ 50 or 100 eV above the peak, the Shirley contribution must banish at those energies. Therefore, the Shirley signal begins as a step-like function at the peak position to then vanish at higher binding energies (examples of the Shirley-signal in the entire range will be presented).

We showed that the Shirley part of the background is related to the capture of photons by deeper levels [5]. The physical process can be described as interchannel coupling [6] but adding a strong involvement of the valence band, i.e., a process resembling off-resonant participator photoemission with the generation of a shake-off type signal. Based on this model, we will present an approximate method to estimate the Shirley signal in the near-peak region.

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10:40am **AS-MoM8 XPS Spectra and Bonding In Ionic Transition Metal Compounds*, C. Richard Brundle,*** C. R. Brundle and Associates*; P.S. Bagus,* University of North Texas

In previous work, [1-3] it has been shown that the cation 2p XPS can reflect the extent of the covalent bonding between the metal cation and the ligands in formally fully ionic TM compounds (ie a nominal "oxidation state"). In the present work, the dependence of the 3p XPS on the covalent character and the charge state of the cation is compared to 2p for selected oxides and halides. The objective is to determine the extent to which the 3p XPS can be used to identify the open shell occupation of the cation; i.e., the nominal oxidation state. It is also of concern to show how the covalent character of the compound modifies the 3p XPS from that for an ideal, isolated, atomic cation. The systems that have been examined include Mn and Fe oxides and halides which are compared with experiment, with each other, and with the calculated XPS of isolated Mn and Fe cations. For the theoretical results, ab initio wavefunctions, WF, have been determined and have been used to obtain the energies and intensities of the cation 2p and 3p XPS. The compounds are modelled with embedded clusters [4] and the WFs are solutions of the Dirac-Coulomb Hamiltonian. Implications for the limitations of quantitation, both elemental and chemical compound, using XPS peak intensities together with standards or theoretical cross-sections, are also discussed

1. C. J. Nelin, P. S. Bagus, C. R. Brundle, E. S. Ilton, and K. M. Rosso, J. Chem. Phys. (to be submitted).

2. P. Bagus, C. R. Brundle, and C. J. Nelin, J. Chem. Phys. (to be submitted).

3. P.Bagus, C. R. Brundle, and C. J. Nelin, presented at the AVS International Symposium, 2017

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

11:00am **AS-MoM9 Combinatorial Group XPS Analysis of Novel Material Systems*, Sarah Coultas,*** Kratos Analytical Ltd, UK*; J.D.P. Counsell,* Kratos Analytical Limited, UK*; C. Moffitt,* Kratos Analytical Inc.*; C.J. Blomfield, A.J. Roberts,* Kratos Analytical Limited, UK

The combinatorial approach has been used widely to discover new material phases for many years now, allowing rapid exploration of composition–structure properties in complex material systems[1]. Compositional mapping is central to obtaining comprehensive pictures of material systems and mapping active chemical properties such as oxidation state and alloying as a function of composition is an integral part of understanding the underlying physical and chemical mechanism of the properties. Here we will apply the traditional approach of combinatorial techniques to explore several model systems using X-ray photoelectron spectroscopy XPS demonstrating the use of group analysis for two different application - ternary alloy formation post thin-film deposition and polymer microarray biomaterial screening.

Ternary metal compounds are used in a wide range of applications; as high-performance alloy materials and electronic semiconductors. We have examined a range of thin-films of first-row transition metals co-deposited on wafers to form a matrix of ternary alloys. The surface composition was analysed with XPS to determine the stoichiometric mixing for different alloy compositions and the extent of oxidation and chemical bond formation during deposition. Further analysis of large datasets allows the user to determine areas of particular interest and performance for further investigation – leading onto more detailed bulk/surface comparison studies using depth profiling techniques. Combinatorial methods will also be exploited for screening of functional biomaterials. The surface composition of a series of polymer microarrays are analysed with XPS to correlate differences in surface chemistry with specific biological performance. This high throughput method allows for library databases to be created for parallel screening of a wide range of polymer blends.

Workflow and data-handling will be discussed for the different systems as will illustrations and set analyses.

C. J. Long, J. Hattrick-Simpers, M. Murakima, R. C. Srivastava, I. Takeuchi, V.L. Karen and X. Li, *Rev. Sci. Inst.,* 78, 072217, 2007.

11:20am **AS-MoM10 Towards Spatially Resolved Quantification of Gold Nanoparticles Embedded in an Organic Matrix using Secondary Ion Mass Spectrometry*, Shin Muramoto*,** *J. Bennett,* National Institute of Standards and Technology (NIST)

Secondary ion mass spectrometry (SIMS) has been successfully used to detect metal nanoparticles in a wide array of organic matrices such as in biological cells, tissue, and within polymer films. However, there are also instances when the nanoparticles cannot be detected at all, presumably due to a combination of charge competition with salts, sample charging, type of primary ion source, and ion dose density. For example, 150 nm Au nanoparticles (AuNPs) embedded in soil nematodes could easily be detected and resolved in a dynamic SIMS instrument using a Cs^+ ion source with a secondary ion yield of 10^{-12}, but no signal could be generated when a ToF-SIMS instrument equipped with a Bi_3^+ ion source was used, even when the sample was covered with a layer of Cs to enhance signal. To test what factors influence the ionization of AuNPs and to identify the ion dose density threshold for detection, a test sample was prepared through inkjet-printing of precisely measured amount of AuNPs onto porcine skin gelatin, a surrogate for biological tissue. By systematically changing the chemistry of the AuNP solution with solutes such as salts, it is possible to see their effect on nanoparticle ionization. The test sample can also be used for the quantification of nanoparticles by changing their concentrations, and see the effects of depth profiling in quantification by changing the distribution of nanoparticles in 3-dimensional space or position inside the film. The ultimate objective of this study is to create a test sample for the spatially resolved quantification of nanoparticles in a biologically relevant environment, to be able to quantify the number of particles in a given area without resorting to high lateral resolution instruments. The effort will also develop SIMS instrumentation into a tool that can be used for determining the pharmacokinetics and biodistribution of nanoparticles in tissue. Preliminary analysis using a ToF-SIMS instrument with a Bi_3^+ ion source showed that the mere presence of gelatin reduced the secondary ion yield of AuNPs by an order of magnitude. In addition, increasing the concentration of Na^+ from 10^{-6} M to 10^{-3} M led to a rather linear decrease in the secondary ion yield from 10^{-13} to 10^{-15}, consistent with the effect of salts on analyte response in an electrospray ionization system. [1] For the dynamic SIMS, the presence of gelatin had no noticeable effect on secondary ion yield of the nanoparticles.

[1] Constantopoulos, T. L.; Jackson, G. S.; Enke, C. G. Effects of Salt Concentration on Analyte Response using Electrospray Ionization Mass Spectrometry. 1999, , 625-634.

11:40am **AS-MoM11 Correction-Free Analysis of SIMS Data at High Mass Resolution in the Presence of Detector Saturation*, Lev Gelb*,** *A.V. Walker,* University of Texas at Dallas

We present a strategy for analyzing TOF SIMS data sets affected by detector saturation at high mass resolution. The detectors used in many instruments undercount ions due to saturation effects; if two or more ions arrive within a very short interval (the “dead time”) only the first to arrive is recorded. This changes both the total number of ions collected and their statistical distribution. The dead time is typically short enough that only ions of the same nominal mass are affected, but a significant fraction of the total ions reaching the detector may still be missed; at low masses the great majority of ions often go undetected. Methods are available for “correcting” the collected spectra at both unit-mass and high-mass resolutions based on an assumed model for the behavior of the detector, but these are problematic when the number of scans taken is small and/or the saturation is sufficiently high. Calculation of the variance of the corrected data as required in many multivariate analysis techniques is also complex. As a result, performing quantitative analysis of TOF SIMS data while preserving high mass resolution remains problematic.

Rather than attempt to correct the measured data to remove saturation, we incorporate the detector behavior into the statistical distribution used in maximum *a posteriori* reconstruction, justified on Bayesian grounds. Essentially, this method finds the *most probably correct* spectra, given the observed data and available prior information. This approach has several advantages over previous techniques: no approximations are involved other than the assumed model of the detector, the method performs well even when applied to highly saturated and/or single-scan data sets, and it is possible to calculate uncertainty estimates for the extracted quantities. Our method is first demonstrated by application to individual spectra. The correctness of the approach and its efficacy are demonstrated on synthetic data sets, and then applied to selected experimental results. Performance on data of different degrees of saturation and/or total number of counts is determined and compared with existing correction-based approaches; the effects of dead-time duration on lineshape and FWHM are also explored. We then demonstrate extension of this approach to imaging data and compare and contrast the results obtained with analyses performed at unit-mass resolution.

Spectroscopic Ellipsometry Focus Topic
Room 202A - Session EL+AS+EM-MoM

Application of SE for the Characterization of Thin Films and Nanostructures

Moderators: Alain C. Diebold, SUNY Polytechnic Institute, Mathias Schubert, University of Nebraska-Lincoln

8:20am **EL+AS+EM-MoM1 Stealth Technology-based Terahertz Frequency-domain Ellipsometry*, Vanya Darakchieva*,** Linköping University, Sweden **INVITED**

We present the newly designed Terahertz (THz) frequency-domain spectroscopy (FDS) ellipsometer at the Terahertz Material Analysis Center (THeMAC) at Linköping university and demonstrate its application to a variety of technologically important materials and heterostructures. We show that employing concepts used in stealth technology for the instrument geometry and scattering anti-static coating, and modulation of the backward wave oscillator (BWO) THz source allows for effective suppression of standing waves enabling accurate ellipsometry measurements with high spectral resolution (of the order of MHz). We further demonstrate an etalon-based method for frequency calibration in THz FDS ellipsometry. The instrument can incorporate various sample compartments, such as a superconducting magnet, in-situ gas cells or resonant sample cavities, for example. Reflection and transmission ellipsometry measurements over a wide range of angles of incidence for isotropic (Si) and anisotropic (sapphire) bulk samples are presented together with determination of the material dielectric constants. We further demonstrate results from cavity enhanced THz optical Hall effect experiments on an AlGaN/GaN high electron mobility transistor structure (HEMT), determining the free charge carrier density, mobility and effective mass parameters of the 2D electron gas (2DEG) at room temperature. We show through in-situ experiments on epitaxial monolayer graphene exposed to different gases and humidities that THz FDS ellipsometry is capable of determining free charge carrier properties and following their changes upon variation of ambient conditions in atomically thin layers. Exciting perspectives of applying THz FDS ellipsometry for exploring low-energy excitation phenomena in condensed and soft matter, such as the vibrational, charge and spin transport properties of magnetic nanolaminates, polymers and hybrid structures for photovoltaics and organic electronics; and determination of THz optical constants and signatures of security and metamaterials are envisioned.

9:00am **EL+AS+EM-MoM3 Spectroscopic Ellipsometry and Finite Element Modeling based Optical Characterization of Highly Coherent Au-Si Slanted Columnar Periodic Nanostructures*, Ufuk Kilic*,** University of Nebraska-Lincoln*; A. Mock,* Linköping University, Sweden*; R. Feder,* Fraunhofer IMWS, Germany*; D. Sekora, M. Hilfiker, R. Korlacki, E. Schubert, C. Argyropoulos, M. Schubert,* University of Nebraska-Lincoln

An unprecedented and phenomenal control of anisotropic optical properties of a material is reported here by utilizing periodic arrangement of nanostructures. These artificially engineered structures exhibit distinct optical, mechanical, and magnetic properties when they are compared with their bulk counterparts which has recently gained a growing interest due to its potential applications in various optical and optoelectronic systems such as lenses, solar cells, photodetectors, and sensors [1-3]. In addition to the material choices (ie. elemental composition), the size and shape of these artificial structures also play a key role in tailoring the aforementioned inherent properties.

Unraveling the mechanisms that influence and control the optical properties of highly-porous, periodic, and three-dimensional arrangements of nanoplasmonic structures can offer new approaches for the development of next generation sensors. Glancing angle deposition and atomic layer deposition can be used to create periodic nanostructures with multiple constituent materials, so-called heterostructured metamaterials.[4] In this study, we employ a two-source (ie. Au and Si) electron-beam-evaporated, ultra-high-vacuum glancing angle deposition which allows for the fabrication of highly-ordered and spatially-coherent super-lattice type Au-Si slanted columnar heterostructured thin films. We perform a combinatorial spectroscopic generalized ellipsometry and finite-element method calculation analysis to determine anisotropic optical properties. We observe the occurrence of a strong locally enhanced dark quadrupole plasmonic resonance mode (bow-tie mode) in the vicinity of the gold junctions, with a tunable and geometry dependent frequency in the near-infrared spectral range. In addition, inter-band transition-like modes are observed in the visible to ultra-violet spectral regions. We demonstrate that changes in the index of refraction due to the concentration variation of a chemical substance environment (gaseous or liquid) within a porous nanoplasmonic structure can be detected by transmitted intensity alterations down to 1 ppm sensitivity.

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9:20am **EL+AS+EM-MoM4 Temperature Dependent Dielectric Function and Critical Point Comparison of bulk Ge and α-Sn on InSb*, Rigo Carrasco,* *C. Emminger, N. Samarasingha, F. Abadizaman, S. Zollner,* New Mexico State University

Germanium is an indirect bandgap semiconductor with a bandgap of 1.55 µm at room temperature. Its band gap can be shifted to longer wavelengths and becomes direct by adding 5-20% Sn, which allows to detect efficiently in the IR range. Alloys of Ge and Sn are therefore of interest for photovoltaics, detectors and room temperature lasers (2-7 µm). Alpha-tin on the other hand, is a semimetal that, when under strain, has a very small band gap at the Gamma point of the Brillouin zone. We compare this direct band gap (E_0 peak) occurring in the infrared region of strained α-Sn on InSb to the absorption edge of Ge.

We investigate the temperature dependence of the complex dielectric function (DF) and interband critical points (CPs) of bulk Ge between 10 and 738 K using spectroscopic ellipsometry in the spectral range from 0.5 to 6.3 eV at a 70° angle of incidence [1]. The complex dielectric function at each temperature is fitted using a parametric oscillator model. Figure 1 shows that variations in temperature influence structures in the spectra of the DF. Furthermore, we analyze CPs in reciprocal space by studying Fourier coefficients as described in [2]. The peaks of the E_0 and $E_0+\Delta_0$ CPs are relatively narrow (Fig. 2) which makes the analysis of their broadenings difficult. A small excitonic peak is visible at the absorption edge E_0, also shown in Fig. 2.

Spectroscopic ellipsometry measurements were also performed on several epitaxially grown α-Sn layers on InSb in the spectral range of 0.03 to 6.5 eV. Comparing the results of the pseudo-dielectric function of Sn to the one of Ge shows a remarkable difference of both spectra in the IR- region, as demonstrated in Fig. 3. While structures at higher energies, such as the E_1 and $E_1+\Delta_1$ CPs, are similar in shape and amplitude for both materials, the E_0-peak in α-Sn is significantly larger than in Ge. Therefore, we believe that the E_0 peak in the spectrum of Sn is not due to excitons but can probably be explained by other parameters which influence the band structure, such as strain, composition, or free carrier concentration. The large peak between E_0 and E_1 is an interference fringe. We also compare the temperature dependence of the E_0 gap in Ge and alpha-tin.

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9:40am **EL+AS+EM-MoM5 Elastomer Thin Films and Conducting Nanostructures for Soft Electronics and Dielectric Elastomer Transducers*, Bert Müller*,** *B. Osmani, T. Töpper,* University of Basel, Switzerland

Nanometer-thin polymer films are essential components of low-voltage dielectric elastomer transducers and will, for example, play a vital role in future artificial muscles [E. Fattorini et al.: Ann. Biomed. Eng. 44 (2016) 1355]. Organic molecular beam deposition (MBD) is a versatile technique to prepare silicone films under well-defined conditions [F. M. Weiss et al.: Mater. Design 105 (2016) 106; T. Töpper et al.: APL Mater. 4 (2016) 056101], but the achievable growth rates of about 1 µm per hour are too low for the fabrication of multi-layer devices. Therefore, we have developed electro-spraying as an alternative deposition method with one or two orders of magnitude faster rates [F. M. Weiss et al.: Adv. Electron. Mater. 2 (2016) 1500476; F. Weiss et al.: Langmuir 32 (2016) 3276]. For the two approaches, spectroscopic ellipsometry (SE) has been employed for in situ monitoring the film's optical properties, the film thickness and the surface morphology during deposition and ultra-violet (UV) light irradiation. The derived quantities were verified by means of atomic force microscopy (AFM). Subsequent to the silicone deposition and the cross-linking by UV light curing, Au has been deposited using MBD and sputtering. This deposition process was also quantitatively characterized using SE and controlled by means of the plasmonic fingerprints of the metal nanostructures [T. Töpper et al.: Adv. Electron. Mater. 3 (2017) 1700073]. The ex situ AFM measurements revealed well-known modulations characteristic for strained surface layers [B. Osmani et al.: Eur. J. Nanomed. 9 (2017) 69]. Recent nano-indentation tests have demonstrated that the Au-layers on the silicone near the critical stress regime hardly contribute to the overall elastic modulus and are, therefore, a sound basis for smart electrodes [B. Osmani et al.: Adv. Mater. Technol. 2 (2017) 1700105]. The nano-mechanical probing of the powered thin-film dielectric elastomer transducers evidenced the importance of the thickness homogeneity for such devices [B. Osmani et al.: Appl. Phys. Lett. 111, (2017) 093104]. The function of planar thin-film dielectric elastomer transducers can be precisely determined taking advantage of the cantilever bending approach [B. Osmani et al.: Rev. Sci. Instrum. 87 (2016) 053901]. Spectroscopic ellipsometry and advanced atomic force microscopy with nano-indentation capability enables us to thoroughly characterize the film morphology as well as the optical and local mechanical parameters of silicone and Au/silicone nanostructures.

10:00am **EL+AS+EM-MoM6 Spectroscopic Ellipsometry Investigation of Temperature Effects in Heated Self-organized 2D Arrays of Au Nanoparticles*, Michele Magnozzi,*** *M. Ferrera, M. Canepa,* Università di Genova, Italy*; F. Bisio,* CNR-SPIN, Italy

Metal nanoparticles (NPs) have the interesting property of behaving as efficient converters of EM radiation into heat. While this can occur via interband photoexcitation, the presence of a Localized Surface Plasmon Resonance provides an extra degree of freedom to tune and optimize the heating [1].

Assessing the temperature of plasmonic NPs during or immediately after illumination is not an easy task, and typically involves the use of models that necessarily have to simplify the complex temperature-dependent dielectric and thermodynamic response of nanosystems; for this reason, a measurement of the T-dependent optical behavior of the NPs at well-defined, externally controlled T would greatly contribute towards a better understanding of the thermoplasmonic properties of metal NPs.

Spectroscopic ellipsometry (SE), being a high-sensitive and non-destructive technique, is an ideal tool to investigate the optical response of NPs systems, provided that a proper model is used for data analysis.

We report a T-dependent investigation of the optical response of densely-packed 2D arrays of gold nanoparticles supported on an insulating nanopatterned substrate [2]. SE measurements were acquired in the 245-1450 nm spectral range, under high-vacuum conditions and in the 25-350 °C temperature interval [3]. Using a dedicated effective medium approximation developed for this kind of systems [2], we are able to reproduce the complex anisotropic optical response of this system employing morphological parameters deduced by *ex-post* AFM analysis; the temperature-dependent dielectric functions of Au, required as input in the model, was obtained in a dedicated SE measurement. The model yields a very good agreement with experimental data at relatively low T; however, though the appropriate T-dependent dielectric function of Au is systematically employed, the model is no longer able to reproduce the data obtained at the highest T. Indeed, a satisfactory agreement is attained introducing an effective correction to the Drude term of the dielectric function of Au, that keeps into account morphological effects affecting the NPs surface - such as softening or melting - that enhance the surface electron scattering rate. Our analysis thus shows that the T-dependent optical properties of metal NPs deviate from simplified expectations, and validate SE as valuable tool to study the complex, anisotropic properties of plasmonic NPs systems.

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10:40am **EL+AS+EM-MoM8 Spectroscopic Ellipsometry of 2D WSe_2 Films*,* *Baokun Song*,** *H.G. Gu, M.S. Fang,* Huazhong University of Science & Technology, China*; Y.L. Hong, W.C. Ren,* Shenyang National Laboratory for Materials Science Institute of Metal Research Chinese Academy of Sciences, China*; X.G. Chen, S.Y. Liu,* Huazhong University of Science & Technology, China

Recently, two-dimensional (2D) WSe_2 has become a popular choice for nanoelectronic, optoelectronic, and valleytronic devices due to its layer-modulated bandgap, high mobility (~200cm^{2}V^{-1}s^{-1}) and on-off ratio (10^8), and large spin-orbit coupling effect. The performance of those novel WSe_2-based devices strongly depends on the intrinsic optical properties of WSe_2, which exhibit an intriguing layer dependency. Therefore, the accurate and quantitative characterization of the layer-dependent optical properties of WSe_2 is essential to the optimal design of those related devices.

In this work, the dielectric function, bandgaps, and critical points (CPs) of WSe_2 ranging from monolayer to bulk have been comprehensively investigated and analyzed by spectroscopic ellipsometry over an ultra-broad band (0.73-6.42eV). The dielectric function of high-quality uniform WSe_2 specimens prepared by chemical vapor deposition were firstly obtained from the ellipsometric spectra. Then the bandgaps of the WSe_2 films were determined from their corresponding absorption coefficient spectra. We experimentally observed that the bandgaps of the $WSe\text{-}_2$ films change from 1.63eV in monolayer to 1.21eV in bulk. Moreover, by using the CPs analysis, a series CPs (A-H) in the dielectric function spectra were precisely distinguished and many of them were rarely reported before. The positions of CPs (A-E) exhibit an obvious red shift when the layer number increases, while the CPs (F-H) exhibit a slight blue shift. The former phenomenon can be partly interpreted as the decaying geometrical confinement of excitons, while the underlying reasons for the latter merit further studies. These novel and advanced optical features will promote the fundamental understanding of the electronic structures and the development of WSe_2-based devices.

11:00am **EL+AS+EM-MoM9 Thermal Evolution Process of $MaPbI_3$ Film Based on Spectroscopic Ellipsometry***, X.Q. Wang, X.Y. Shan, H. Siddique,* ***Rucheng Dai****, Z.P. Wang, Z.J. Ding, Z.M. Zhang,* University of Science and Technology of China

Thermal Evolution Process of $MaPbI_3$ Film Based on Spectroscopic Ellipsometry

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Abstract

During the last few years, the hybrid organic-inorganic methylammonium lead halide perovskite $CH_3NH_3PbI_3$ ($MaPbI_3$) has received great interest in the field of photovoltaics [1,2]. The relevant researches develop rapidly since the first realization of organic-inorganic hybrid solar cell, due to the excellent performance of $MaPbI_3$, such as high charge mobilities, suitable band gap and long carrier diffusion length. However the stability of MaPbI has been a key issue hinder the practical application [3]. Here we present in-situ spectroscopic ellipsomety measurement to understand the nature of thermal degradation process of MaPbI . The dynamic evolution process of dielectric constants of the as-prepared $MaPbI_3$ film through heating is obtained by an effective medium approximation model fitting. The proportion of $MaPbI_3$ and PbI is also obtained from the analysis of the ellipsometry data. The thickness of the film decrease in two-step, which is explained as the collapse of the PbI_2 frame. Our work provide the first in-situ detection of the optical properties through the degradation process of $MaPbI_3$ film, which can be consulted for further improving the stability of $MaPbI_3$.

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11:20am **EL+AS+EM-MoM10 a-Si as a Protective Layer to Block the Oxidization of Al mirrors*, Yhoshua Wug,*** University of California at Los Angeles*; D.D. Allred, R.S. Turley,* Brigham Young University

Arguably, the best path to produce a truly broadband, e.g., an IR-optical-UV-EUV (extreme ultraviolet) mirror, for a future space observatory is an EUV multilayer mirror coated by a very thin bare aluminum layer. However, using a bare Al layer presents challenges that first must be overcome. Al oxidizes rapidly when contact with the atmosphere occurs. The customary solution is to cover the mirror with a protective evaporated fluoride layer. Unfortunately, these are opaque under ~110 nm, whereas, bare Al itself is highly reflective down to 85nm and could be used as a mirror to that wavelength if a barrier were not required. Once the mirror is in space far from the Earth, where there is no oxygen, Al would no longer need a barrier layer. Could a barrier be removed in space? Neither fluorides nor aluminum oxide can be removed once they are deposited without damaging the mirror’s surface and destroying VUV reflectance. a-Si could be used as a protective layer that is potentially removable without roughening the Al surface. Dry hydrogen etching processes exist that could remove a silicon barrier as silane gas which would dissipate quickly in space. Such a process would use the Al layer as an etch stopping barrier in removing the a-Si protective layer. But is a-Si a suitable barrier for Al? We report our variable-angle spectroscopic ellipsometry studies of evaporated a-Si thin films on evaporated Al films. We discuss the conditions where a-Si can act as a protective layer to block aluminum oxidation.

11:40am **EL+AS+EM-MoM11 Terahertz to Mid-infrared Dielectric Response of Poly-methacrylates for Stereolithographic Single Layer Assembly***, D.B. Fullager,* ***Serang Park****, Y. Li, J. Reese,* University of North Carolina at Charlotte*; E. Sharma, S. Lee,* Harris Corporation*; S. Schöche, C.M. Herzinger,* J.A. Woollam Co. Inc*; G.D. Boreman, T. Hofmann,* University of North Carolina at Charlotte

Producing THz optical components with arbitrary shapes using additive manufacturing is receiving considerable interest because it offers a rapid, low-cost avenue for THz imaging system development. In order to design such THz optical components appropriately, accurate knowledge of the complex dielectric function of the materials used for stereolithographic 3D fabrication, is crucial. In this presentation we report on the complex dielectric function of several poly-methacrylates which are frequently used for stereolithographic fabrication. Spectroscopic ellipsometry data sets from the THz to mid-infrared spectral range were obtained from isotropically cross-linked poly-methacrylate samples. The data sets were analyzed using stratified layer optical model calculations using parameterized model dielectric functions. While the infrared spectral range is dominated by several strong absorption features with Gaussian profiles, these materials are found to exhibit only weak absorption in the THz range. In conclusion we find that thin transmissive THz optics can be easily achieved using poly-methacrylate-based stereolithographic fabrication. Possible origins of the observed absorption in the THz spectral range are identified and pathways to reduce it are discussed.

Electronic Materials and Photonics Division
Room 101A - Session EM+MP+PS-MoM

IoT Session: CMOS, Beyond the Roadmap and Over the Cliff

Moderators: Sean King, Intel Corporation, Wilman Tsai, Taiwan Semiconductor Manufacturing Company (TSMC)

8:20am **EM+MP+PS-MoM1 Aluminum Gettering Gate for Improving Defect Density in SiGe MOSCAP Devices***, **Emily Thomson**, M. Kavrik, A.C. Kummel,* University of California at San Diego

The use of SiGe alloys in place of silicon in semiconductor devices has been anticipated for many years due to its high carrier mobility and tunability of the band gap by varying Ge content. However, widespread use of SiGe in industry has been prevented by the presence of interface defects between the SiGe and oxide layer in MOSCAP devices. It has been shown that Ge-Ox bonds at the interface are the main source of these defects so by encouraging SiOx bonds or discouraging GeOx bonds, interface defects can be minimized. The higher heat of formation of SiOx compared with GeOx allows for the selective destruction of GeOx bonds using an oxygen scavenging metal as the gate metal, causing oxygen from GeOx bonds to diffuse through the oxide layer. Here, aluminum was used as an oxygen scavenging gate in order to achieve a low defect density of 3E11 $eV^{-1}cm^{-2}$. The high-k dielectric HfO_2 was deposited using atomic layer deposition with precursors TDMAH (tetrakis (dimethylamido) hafnium) and H2O and the aluminum gates were deposited using thermal evaporation. MOSCAP devices with nickel gates were fabricated and measured in parallel to show contrast with a non-scavenging gate metal. C-V measurements were used to characterize interface defect density. TEM images confirmed oxygen scavenging by showing a silicon rich SiGe-oxide interface and an Al2O3 layer at the HfO2-Al gate interface.

8:40am **EM+MP+PS-MoM2 Direct Growth of Single Crystal Compound Semiconductor Materials on Diverse Substrates for Beyond the Roadmap Multifunctional Integrated Circuits***, **Debarghya Sarkar**, R. Kapadia,* University of Southern California

Technological advancement in semiconductor devices for the past several decades has been mainly driven by scaling device dimensions to achieve high computational density and thus operational bandwidth. The next generation of technological advancement is likely to come from vertical fine-grain integration of multiple materials for 3D multifunctional integrated circuits. Epitaxial lift-off and transfer processes are currently employed towards realizing such structures, which though successful, have several shortcomings. On the other hand, direct growth of technologically relevant materials on amorphous dielectrics using state-of-the-art vapor-phase crystal growth techniques results in polycrystalline films with uncontrolled morphology unsuitable for high performance devices. As a potential solution addressing these issues, here we report the recent advances made in the templated liquid phase (TLP) growth technique that enables growth of large-area single crystals of compound semiconductors directly on diverse non-epitaxial substrates. We demonstrate growth of optoelectronic materials such as binary III-V InP and InAs, and optical bandgap tuning with ternary III-V materials like InGaP. We also show phase-controlled growth of binary IV-V materials such as Sn_4P_3 and SnP for high capacity anode materials in Li and Na ion batteries. Further, as the first step towards directly integrating multiple materials on the same substrate, we demonstrate atomically-sharp lateral heterojunctions of cubic InP and rhombohedral Sn_4P_3 crystals. We grow these materials in selective area with deterministic template geometry and conformal to underlying device nanostructures on any thermally stable crystalline (Gd_2O_3), amorphous (SiO_2, Si_3N-_4, TiO_2, and $Al-_2O_3$), or 2D (graphene) substrate. Despite grown on non-epitaxial substrates, the materials have been characterized to have high quality crystallinity, with high optoelectronic quantum yield irrespective of the substrate, and high carrier mobility. These demonstrations potentially mark the beginning of a new genre of material growth technique with increased opportunity for electronic, photonic, optoelectronic and energy devices, and system design with novel functionalities.

10:00am **EM+MP+PS-MoM6 Surface Free Energy and Interfacial Strain in HfO2 and HZO Ferroelectric Formation***, **Andrew Kummel**, E. Chagarov, M. Kavrik,* University of California at San Diego*; M. Katz, N. Sanford, A. Davydov,* National Institute of Standards and Technology (NIST)*; M. Lee,* National Taiwan University

The mechanism of stability of the phases of HfO_2, ZrO_2, and HZO ($Hf_xZr_{1-x}O_2$) were systematically investigated with density functional theory molecular dynamics (DFT-MD). For the bulk states, the monoclinic phase ("m") is about 80 mV per formula unit more stable than either the orthorhombic ferroelectric ("f") phase or tetragonal (t-phase) for all three oxides. The surface free energies of the (001), (110), and (111) surfaces of all three oxides were calculated using an identical DFT technique. For all three oxides, the (111) face has the lowest surface free energies consistent with experimental data on columnar HZO grains showing [111] is the preferred growth direction. However, the surface free energy for all direction are nearly degenerate between HfO_2, ZrO_2, and HZO; therefore, even for nanocrystal formation the surface free energy does not favor f-phase formation. The effect of stress/strain was calculated by determining the free energy of formation as a function of the volume of the unit cell. When the oxides are grown in the low density amorphous phase but a post deposition anneal is perform for crystallization. The crystalline forms are more dense than the amorphous forms and the DFT calculation show that a higher surface area per unit cells will greatly favor f-phase formation. However, the effect is nearly identical for HfO_2, ZrO_2, and HZO; this is consistent with experiments showing the molar volumes of HfO_2 and ZrO_2 being within 2%. Instead, formation of nanocrystalites is hypothesized to be the source of the enhanced processing window for HZO. Experimental data is consistent with partial phase separation in HZO. Atom probe tomography imaging of the chemical composition of TiN/5 nm HZO/Si(001) ferroelectric films show an asymmetric distribution of the Hf and Zr within the HZO layer with the Zr being concentrated near the TiN/HZO interface; this is consistent with ZrO_2 having a 100C lower crystallization temperature than HfO_2 and therefore initiate the crystallization starting on the TiN(111) surface. It is hypothesized that the nanocrystals which template on TiN(111) can produce the interfacial stress/strain needed to stabilize f-phase formation; high resolution TEM shows regions of epitaxial alignment between HZO and TiN consistent with this mechanism. In addition atom probe tomography (APT) was performed on TiN/HZO/Si structures to determine the film composition of the interfaces for indication of possible phase separation of HZO since phase separation could promote nanocrystal formation.

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10:40am **EM+MP+PS-MoM8 The Role of Selective Processes in the Atomic Scale Era***, **Robert Clark**, J. Smith, K.-H. Yu, K. Tapily, G. Pattanaik, S. Consiglio, T. Hakamata, C.S. Wajda, A. Raley, G.J. Leusink,* TEL Technology Center, America, LLC **INVITED**

The semiconductor industry has reached the point where devices are approaching atomic scales. But continued scaling presents a number of new challenges to our industry. First, there is no longer plenty of room at the bottom, which has forced device makers to scale upward by adopting three dimensional device structures and architectures. This has resulted in a drastic increase in the aspect ratios encountered during chip manufacturing. In addition, even with the advent of EUV lithography it will be necessary to employ multi-patterning technologies in order to fabricate the sub-lithographic features necessary to scale further. Multi-patterning requires multiple masks per layer which presents a challenge in terms of aligning masks to each other within a layer, and from layer to layer as the chip is fabricated. Self-aligned process flows such as self-aligned blocks, fully self-aligned vias, and self-aligned contacts are being employed to increase the margin of allowable edge placement error (EPE) for aligning feature and layers to each other at the cost of additional process complexity as well as exacerbating the problem of ever-increasing aspect ratios. Finally, functional films at useful thicknesses need to be accommodated within the volume of the device without voids or seams that can impact chip yields through degraded electrical performance or by providing a source of particles or foreign material.

To overcome these difficulties it is necessary to begin transitioning from the current top down manufacturing paradigm to a bottom up or additive manufacturing style. Selective depositions and etches represent a path to make this transition for devices makers. Self-aligned process flows already make use of etch selectivity between materials in order to achieve feature self-alignment, but isotropic and anisotropic selective depositions can provide additional advantages. Because area selective depositions are inherently self-aligned to the target material, they can enable new process flows for self-alignment. In addition, anisotropic feature filling can be used to fill high aspect ratio, or reentrant features on the chip without deleterious voids and seems as well as reducing the overburden needed for chemical mechanical polishing (CMP). And selective depositions can also be used to avoid or relieve the crowding of functional films within devices or other structures. In this presentation we seek to illustrate, with examples of new processes currently under investigation, how selective depositions and etches can enable future manufacturing nodes by introducing additive processing into the manufacturing flow.

11:20am **EM+MP+PS-MoM10 Selective Patterning of Silicon/Germanium Surfaces and Nanostructures via Surface Initiated Polymerization***, **Amar Mohabir**, T. Weiss, G. Tutuncuoglu, E.M. Vogel, M.A. Filler,* Georgia Institute of Technology

Functional devices (e.g., transistors) require controlled compositional heterogeneity and hierarchy at the nanoscale. When such devices are to be produced at very large throughputs (e.g., large-area integrated circuitry), an alternative to top-down patterning is necessary to define key features. Here, we show how surfaces exhibiting Si and Ge domains can be selectively masked using the surface-initiated growth of polymer films. Our approach is particularly useful for the patterning of, and subsequent deposition on, 3-D nanostructures, such as Si/Ge nanowire heterostructures. Such structures exhibit a variety of exposed facets that complicates direct (i.e., without a mask) area selective deposition approaches. Surface masking of Si, but not Ge, domains is accomplished by attaching an initiator to the surface followed by the atom transfer radical polymerization of polymethylmethacrylate (PMMA). Due to differences in initiator density on the Si and Ge regions, the resulting PMMA is approximately 2x thicker on the Si surface. A subsequent hydrogen peroxide etching step removes PMMA on the Ge surface, thus providing nearly 100% selectivity, but leaves the Si regions unaffected. We hypothesize the mechanism of PMMA removal is hydrogen peroxide diffusion through the polymer layer and etching of the underlying Ge atoms. In this study, we use a suite of spectroscopy and microscopy techniques to investigate the effect of initial Si/Ge surface treatment, PMMA polymerization conditions, and hydrogen peroxide etching conditions on the resulting polymer film properties and surface. The ability to selectively mask nanoscale objects in a bottom-up fashion opens up the possibility for nanoscale patterning in a simultaneously high-throughput and cost-effective manner.

11:40am **EM+MP+PS-MoM11 Chemically Selective Imaging of Sequential Infiltration Synthesis with nm-scale Spatial Resolution***, D. Nowak, **Tom Albrecht**,* Molecular Vista

Area selective deposition (ASD) is an active area of research for advanced nanofabrication. Closely related to ASD is sequential infiltration synthesis (SIS) where inorganic material is infused into select polymer material to render an organic/inorganic hybrid material based on a polymer-template. The organic component can be burned or etched away to leave only the inorganic component, which can be used as etch mask or for other purposes. For lithography applications, the length scale (in nanometers range) and the nature of material (organic and inorganic molecules) are such that traditional techniques such as FTIR, electron microscopy, and X-ray scattering are not able to yield real space, chemically selective imaging of SIS processes. Photo-induced Force Microscopy (PiFM) [1] combines infrared (IR) absorption spectroscopy and atomic force microscopy (AFM) via illumination of the tip-sample junction with tunable IR laser light and mechanical detection of forces acting on the tip in response to absorption of light by the sample. By mapping the IR absorption of the sample as a function of IR wavelength and position, nm-scale resolution is achieved in displaying the locations of heterogeneous materials on the surface of a sample. This imaging capability is useful for investigating chemical pre-patterns as well as selectively deposited materials in area-selective processes like block copolymer directed self-assembly, SIS [2], and a variety of area-selective deposition techniques. In this talk, we will present the PiFM results on a model system: Al_2O_3 SIS using trimethyl aluminum and H_2O with poly(styrene-block-methyl methacrylate) (PS-*b*-PMMA) block copolymer with 41 nm full pitch lamellae, demonstrating sub-10 nm spatial resolution of chemically selective imaging.

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Industrial Physics Forum

Room 101B - Session IPF+AS+BI+NS-MoM

Biofabrication: From Tissue to Organ

Moderators: Jason Bardi, American Institute of Physics, Jim Hollenhorst, Agilent Technologies

8:20am **IPF+AS+BI+NS-MoM1 Strategic Thinking on the Architecture and Design of Scaffolds for Regenerative Medicine***, **Buddy D. Ratner**,* University of Washington, Seattle **INVITED**

Scaffolds for use in medicine and biology might be traced back to the 1940's when parachute cloth was first used for vascular prostheses. However, in the mid-1980's scaffolds took off as an essential tool in tissue engineering. This talk will explore some of the basic biology of porosities, roughness and textures on cell responses in vitro and tissue responses in vivo. University of Washington studies will be presented demonstrating enhanced healing and regeneration with precision control of pore structures for in vivo applications. The use of surface techniques and tools will be addressed for decorating the surfaces of scaffolds with biological molecules. Finally, the potential of secondary ion mass spectrometry (SIMS) for analyzing and imaging pore structure will be addressed.

9:00am **IPF+AS+BI+NS-MoM3 Sequential Bottom-up Assembly of Synthetic Cells***, **Joachim Spatz**,* Max Planck Institute for Medical Research, Germany **INVITED**

The evolution of cellular compartments for spatially and temporally controlled assembly of biological processes became an essential step in developing life. Synthetic approaches towards cellular-like compartments are still lacking well-controlled functionalities as would be needed for more complex synthetic cells. In part, this is due to the mechanical and chemical instabilities of the lipid-based protocells and a lack of technical means for their well-controlled manipulation. We developed droplet supported lipid bilayer vesicles by microfluidics to generate mechanically and chemically stable and, therefore, manipulable cell-like compartments with a well-defined chemical and biophysical microenvironment. The enhanced stability enabled the sequential loading of such compartments with biomolecules by pico-injection microfluidics without compromising their functionality as synthetic cells. We demonstrate a successful sequential bottom-up assembly of a compartment with lipids, transmembrane proteins (integrin, F_oF_1-ATP synthase) and cytoskeleton proteins which would not assemble in a fully functional way by mixing and including them in one pot at once

9:40am **IPF+AS+BI+NS-MoM5 Activation of Inkjet Printed Cells Enhances Microvasculature Formation in Host Tissues***, **Thomas Boland**, B. Oropeza, L.H. Solis,* University of Texas at El Paso*; M. Yanez,* University of South Carolina **INVITED**

Bioprinting refers to the co-deposition of cells alongside scaffolding materials to build two- and three-dimensional constructs for tissue engineering applications. The technology faces several limitations that present interesting engineering opportunities. The nature and scope of the problems will be discussed in the context of the fabrication of microvasculature. The current tissue-engineering paradigm is that successfully engineered thick tissues must include vasculature. Studies of membrane properties of thermal inkjet printed cells by evaluating showed normal electrophysiology, but short-term membrane disruptions, which allow small molecular weight molecules to enter. Cell viability was high and apoptotic behavior was not upregulated. Alginate (1%) and gelatin type B (2.5%) constructs or scaffolds were prepared by bioprinting of a crosslinker with endothelial and endothelial / β cells. Control scaffolds were manually pipetted with the same cells and without any cells.Upon implantation the bioprinted endothelial cell constructs showed a nearly ten-fold increase in blood vessels was observed (p= 0.009), a dose response was observed but the β cells seemed to inhibit vessel formation. The explanted implants show large complete vascular features on the H&E and CD31 stains; Immunohistochemistry showed the tissue were regenerated with the human cells that made up a large part of the vasculature. Further insights into how the inkjet printing process activated endothelial cells will be presented. Understanding these processes will improve bioprinting and may eventually lead to creating fully vascularized large soft tissues, which have not been successfully grown thus far.

10:40am **IPF+AS+BI+NS-MoM8 Challenges in Organ-specific Vascular Engineering and Tissue Assembly***, **Ying Zheng**,* University of Washington **INVITED**

Engineered tissues have emerged as promising new approaches to repair damaged tissues as well as to provide useful platforms for drug testing and disease modeling. Outstanding challenges remain in 1) the lack of well-defined and mature cell sources to facilitate translational outcomes and 2) the lack of control over vascular structure and perfusion efficiency in engineered 3D tissue constructs, preventing large-scale tissue fabrication, and leading to insufficient perfusion after implantation in vivo. In this talk, I will present recent progress in my lab in engineering microvasculature from human pluripotent stem cell derived endothelial cells, and their anastomosis *in vitro* and infarcted heart *in vivo*. The eventual goal of this drive is to use the single cell source to derive organ-specific vascular cells and tissue for regeneration. Next I will discuss our work in understanding the human microvascular endothelial cell heterogeneity from four major organs, heart, lung, liver and kidney and describe their distinct structure and function. I will show an example of using human kidney-specific microvascular cells to model kidney specific injury. Finally I will discuss challenges and future perspectives towards engineering human organ-specific tissue models.

11:20am **IPF+AS+BI+NS-MoM10 Bioprinting for Translational Applications: *The Quest for Whole Organ Fabrication, James J. Yoo,*** Wake Forest School of Medicine **INVITED**

Tissue engineering and regenerative medicine has emerged as an innovative scientific field that focuses on developing new approaches to repairing cells, tissues and organs. Over the years, various engineering strategies have been developed to build functional tissues and organs for clinical applications. However, challenges still exist in developing complex tissue systems. In recent years, 3D bioprinting has emerged as an innovative tool that enables rapid construction of complex 3D tissue structures with precision and reproducibility. This developing field promises to revolutionize the field of medicine addressing the dire need for tissues and organs suitable for surgical reconstruction. In this session novel and versatile approaches to building tissue structures using 3D printing technology will be discussed. Clinical perspectives unique to 3D printed structures will also be discussed.

In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic

Room 202B - Session MM+AS+NS+PC-MoM

Mechanical, Electrical, Thermal and Optical Systems for In situ TEM (9:00-10:100 am)/Beam Induced Effects and Processing in Liquid/Gas Cells for TEM/SEM (10:40-11:40 am)

Moderators: Suneel Kodambaka, University of California, Los Angeles, Olga Ovchinnikova, Oak Ridge National Laboratory

9:00am **MM+AS+NS+PC-MoM3 Cantilever Substrates for Quantitative Growth Experiments in the Environmental Transmission Electron Microscope***, **Frances Ross**,* IBM T. J. Watson Research Center, MIT **INVITED**

Environmental TEM is an excellent tool for obtaining quantitative information on growth processes and materials transformations. However, it is essential to measure the local temperature, pressure, and other key conditions at the sample location. Well controlled and accurately calibrated *in situ* experiments often make use of specially designed samples and involve various methods for direct measurement of the reaction parameters. Here we describe some of these strategies, but focus on one particular sample design which we suggest is well suited for experiments addressing chemical vapor deposition. In this sample design, growth takes place at the tip of a hairpin cantilever microfabricated from single crystal silicon and heated by direct current. Epitaxial growth is possible on the cantilever surfaces, and deposition on materials such as amorphous silicon nitride is achieved by first coating the cantilever. We discuss how the local temperature and pressure can be measured by monitoring a calibrated growth process. We also discuss how growth can be examined under more complex environments, such as electric fields, using designs involving multiple cantilevers and actuators. We finally discuss approaches to higher pressure than is possible in conventional ETEM by integrating cantilevers in a closed gas cell. Custom substrates based on microfabricated designs appear poised to expand the possibilities of quantitative *in situ* growth experiments to exciting new regimes and materials systems.

9:40am **MM+AS+NS+PC-MoM5 In Situ Laser Heating and Excitation in the Transmission Electron Microscope: Recrystallization, Grain Growth, Phase Separation and Dewetting in $Ag_{0.5}Ni_{0.5}$ Thin Films***, **Philip D. Rack**,* University of Tennessee Knoxville*; Y. Wu,* University of Notre Dame*; C. Liu,* University of Tennessee Knoxville*; T.M. Moore, G.A. Magel,* Waviks Inc.*; D. Garfinkel,* University of Tennessee Knoxville*; J.P. Camden,* University of Notre Dame*; M.G. Stanford, G. Duscher,* University of Tennessee Knoxville

Motivated by the desire to image excited state and high temperature materials phenomena at the nano and atomic scale, Waviks Inc. has recently developed an in situ optical delivery tool for the (scanning) transmission electron microscope (S)TEM. The tool used in these experiments contains two optical delivery channels and is mounted on a Zeiss Libra 200 (S)TEM system. A 785 nm wavelength laser diode system coupled through a 5 µm mode field diameter single-mode fiber is used to deliver >200 mW to the sample surface. The laser can be gated from a few ns to continuous wave (cw) at repetition rates up to 16 MHz. A second optical channel with a 100 µm core diameter broad spectrum multimode fiber is also available for coupling to any excitation source in the wavelength range from 200 to 2100 nm using a standard SMA fiber connector. The system is mounted to a 3 axis (+/- *x,y,z*) nanomanipulator for focusing to the electron/sample coincident point (with sample tilted at ~45 degrees). The system contains a lens system to re-image the fiber optics (1x) at a working distance of ~10 mm, which is long enough eliminate charging and minimizes re-deposition of material. To demonstrate the functionality of the tool, we will show photothermal annealing results of a supersaturated $Ag_{0.5}Ni_{0.5}$ film. We will demonstrate recrystallization, grain growth, phase separation and solid state dewetting of the films via various laser powers, pulse widths, pulse numbers, laser radius. Finally, we will demonstrate interesting in situ excited state phenomena via electron energy gain spectroscopy of plasmonic silver nanoparticles.

10:00am **MM+AS+NS+PC-MoM6 In situ Transmission Electron Microscopy Study of the Mechanical and Electrical Properties of Single III-V Semiconductor Nanowires***, **Lunjie Zeng**,* Chalmers University of Technology, Gothenburg, Sweden*; C. Gammer,* Austrian Academy of Sciences, Austria*; B. Ozdol,* Lawrence Berkeley National Laboratory*; T. Nordqvist, P. Krogstrup,* University of Copenhagen, Denmark*; A.M. Minor,* Lawrence Berkeley National Laboratory*; W. Jäger, E. Olsson,* Chalmers University of Technology, Gothenburg, Sweden

III-V semiconductor nanowires possess outstanding electronic and mechanical properties that can be utilized in future high-speed electronic devices, solar cells and sensors. To better understand these properties and their relations to the microscopic structure of the nanowires, it is critical to directly correlate the structure and properties of single nanowires. However, the direct characterization of the mechanical and electrical properties of single nanowires, in particular, the correlation between them is still a challenge. In this study, we directly investigate the intrinsic mechanical and electromechanical properties of individual InAs nanowires using in situ transmission electron microscopy (TEM).

Quantitative stress, strain and electrical transport measurements were carried out on single InAs nanowires simultaneously. A Hysitron PI95 nanoindentation TEM holder was used for the in situ TEM study. By using an electrical push-to-pull (EPTP) device in the in situ TEM holder, tensile stress was applied via the nanoindenter in the holder while the force applied on the nanowire was measured by a transducer in the holder. The EPTP device also enables current-voltage (I-V) measurements on single nanowires. Nanoscale lattice strain mapping within the nanowire was performed using scanning transmission electron microscopy (STEM) combined with nanobeam electron diffraction (NBED). NBED diffraction patterns were acquired using a Gatan K2 direct detection camera. Based on the detailed strain and stress measurements, Young's modulus and Poisson's ratio of single InAs nanwires were directly determined. The Young's modulus of single InAs nanowire is smaller than that of the bulk, while the Poisson's ratio of the InAs nanowire is similar as the bulk InAs. The electrical measurements showed that the resistivity of the InAs nanowires decreased continuously with increasing tensile stress. The piezoresistance coefficient of the nanowire was found to be significantly larger than that of bulk InAs. Moreover, significant inhomogeneous strain distribution within the nanowire under stress was unveiled by STEM-NBED strain mapping. The inhomogeneous strain distribution at nanometer scale can increase the resistivity of the nanowire by enhancing electron scattering. The findings demonstrate unique mechanical and electromechanical properties of the nanoscale InAs wires and provide new insights of the correlation between mechanical strain and electrical transport properties in free-standing nanostructures.

Financial support from Swedish Research Council and Nanoscience and Nanotechnology Area of Advance at Chalmers University of Technology are acknowledged.

10:40am **MM+AS+NS+PC-MoM8 Radiolytic Synthesis of Nanostructured Materials using *In situ* Liquid Cell Microscopy***, **Raymond Unocic**, X. Sang, A. Belianinov, O.S. Ovchinnikova, K. More, S. Jesse,* Oak Ridge National Laboratory **INVITED**

There are a wide range of solution-based strategies available for the size- and shape-controlled synthesis of functional nanomaterials for applications in catalysis, energy storage, biomedical, optical, and electronics. To elucidate growth mechanisms, *in situ* liquid scanning transmission electron microscopy (STEM) plays a role for directly imaging and quantifying growth dynamics of nanoparticles from liquid-phase precursors. In this work, we report several strategies for the *active* controlled synthesis of metallic and bimetallic nanoscale architectures using the concept of radiolytic synthesis. In one approach, we developed a direct-write, template-free method to fabricate self-supporting, hollow, metallic nanostructures, and we interpret the formation mechanisms based on direct observations of nucleation and growth. The electron beam used for imaging stimulates radiolysis, promoting the dissociation of water (H_2O) molecules and the formation of complex radical species such as aqueous electrons (e_{aq}^-) and other reducing and oxidizing species. The highly reducing radiolytic species assist in the chemical reduction of metal ions from the precursor solution, resulting in the formation of a metallic nanocrystal seed, which then acts as a catalyst for H_2 gas generation forming a metal encapsulated hollow nanobubble. In another approach, a custom-built electron beam nanopositioning and scan-generator system is used to precisely control the position and electron dose of the focused electron or ion beam to fabricate metallic and bimetallic nanostructured materials. These strategies enable fundamental electron beam interaction studies and open a new pathway for direct-write nanolithography from liquid-phase solutions.

This research was supported by the Center for Nanophase Materials Sciences, which is a United States Department of Energy Office of Science User Facility.

11:20am **MM+AS+NS+PC-MoM10 Electron Beam Induced Cross-Linking in Liquid Hydrogels***, **Tanya Gupta**, A. Kolmakov,* National Institute of Standards and Technology (NIST)

Advances in additive manufacturing of bio-friendly polymeric materials over the last decade has revolutionized the diverse fields like rapid prototyping, tissue engineering, drug delivery etc. The technology currently relies on laser, thermal or UV induced 3D printing. Other triggers with similar effects can in principle be used as ionizing radiation to carry out the crosslinking. In this work we explore the use of electron beam to perform 3-D patterning at mesoscale and explore its potential towards rapid prototyping. In particular, knowledge of electron interaction with the printing ink allows us to predict effect of various control parameters like beam energy , current and dwell time on the topology of the features formed. A Monte-Carlo simulation coupled with a rigorous kinetic model is built to study the interplay of dose distribution, total interaction volume and diffusional effects of the active radiolytic species.

11:40am **MM+AS+NS+PC-MoM11 Nanoscale Chemical Reactor Based on Localized Surface Plasmon Energy in Environmental Transmission Electron Microscope***, **Canhui Wang**[1], W.-C. Yang,* UMD/NIST*; R. Sharma,* National Institute of Standards and Technology

Miniaturizing chemical processes in a research context has many advantages, including the ability to examine the reaction at atomic resolution, the reduced usage of costly and/or hazardous chemical reagents, and the ability to be integrated into analytical devices. [1-2] However, the current efforts of miniaturizing chemical processes have been limited by achievable minimum reaction volume and the lack of precision control over the reaction locations. Herein, we demonstrate a nanoscale chemical reactor utilizing localized surface plasmon (LSP) resonance as the energy source in an environmental transmission electron microscope (ETEM). This approach allows us to confine the reaction within proximity of the nanoparticle while taking advantage of the high spatial resolution capability of the electron microscope to monitor the reaction.

Plasmonic nanoparticles, such as Au or Al, are placed in a reactive environment inside the ETEM. The composition and partial pressure of the gases are controlled by a gas handling system. Electron energy-loss spectra (EELS) imaging is used to acquire both elemental and LSP maps from the same nanoparticle. This allows the mapping and quantification of different gas adsorption on the nanoparticle surface. The energy required for the reaction of interest is provided by the LSP resonance excited by the high energy electron beam. The reaction location is confined within proximity of the nanoparticle due to the local field enhancement of the LSP resonance. Using a non-negative matrix factorization machine learning algorithm [3], we map the energy transfer pathways from the electron beam to the nanoparticle at nanometer spatial resolution and 0.08 eV energy resolution. The temperature distribution of the nanoparticle is monitored with few-nanometer spatial resolution using time-resolved EELS. Reaction processes, including morphological changes and transition of crystalline phases, are monitored using aberration-corrected atomic-resolution movies. By utilizing LSP resonance to initiate the reaction, we show that chemical processes can be confined in a nanometer scale volume, and modulated by electron flux. Important factors of the reaction, including composition of the reactants, adsorption of gases, transfer of energy, change of temperature, as well as reaction dynamics, can be monitored with nanometer or atomic resolution. Our approach paves the way to understanding a wide range of chemical reactions at the atomic scale.

References:

[1] Abdelgawad, Mohamed, et al. Lab on a Chip 9.8 (2009): 1046-1051.

[2] Williamson, M. J., et al. Nature materials 2.8 (2003): 532.

[3] O. Nicoletti, et al. Nature 502.7469 (2013): 80.

Materials and Processes for Quantum Computing Focus Topic

Room 203A - Session MP+EM+MN+NS-MoM

Systems and Devices for Quantum Computing I

Moderator: Vivekananda Adiga, IBM, T.J. Watson Research Center

9:00am **MP+EM+MN+NS-MoM3 Quantum Supremacy: Checking a Quantum Computer with a Classical Supercomputer***, **John Martinis**,* Google Inc **INVITED**

As microelectronics technology nears the end of exponential growth over time, known as Moore's law, there is a renewed interest in new computing paradigms such as quantum computing. A key step in the roadmap to build a scientifically or commercially useful quantum computer will be to demonstrate its exponentially growing computing power. I will explain how a 7 by 7 array of superconducting xmon qubits with nearest-neighbor coupling, and with programmable single- and two-qubit gate with errors of about 0.2%, can execute a modest depth quantum computation that fully entangles the 49 qubits. Sampling of the resulting output can be checked against a classical simulation to demonstrate proper operation of the quantum computer and compare its system error rate with predictions. With a computation space of 2^49 = 5 x 10^14 states, the quantum computation can only be checked using the biggest supercomputers. I will show experimental data towards this demonstration from a 9 qubit adjustable-coupler "gmon" device, which implements the basic sampling algorithm of quantum supremacy for a computational (Hilbert) space of about 500. We have begun testing of the quantum supremacy chip.

9:40am **MP+EM+MN+NS-MoM5 Active Protection of a Superconducting Qubit against Josephson Amplifier Backaction***, **Baleegh Abdo**, N.T. Bronn, O. Jinka, S.B. Olivadese, A. Corcoles, M. Brink,* IBM T. J. Watson Research Center*; R. Lake, D.P. Pappas,* National Institute of Standards and Technology*; J.M. Chow,* IBM T. J. Watson Research Center

Nonreciprocal microwave devices, e.g., isolators and circulators, are key components in high-fidelity, quantum-nondemolition (QND), measurement schemes. They separate input from output and protect the quantum systems from unwanted backaction originated by the output chain. However, state-of-the-art, cryogenic circulators and isolators are disadvantageous in scalable architectures because they are lossy, bulky and use magnetic materials and strong magnetic fields, which are not compatible with superconducting circuits. In this work, we realize and characterize nonreciprocal, superconducting devices suitable for qubit readout, which are formed by coupling two nondegenerate Josephson mixers in interferometric schemes. Nonreciprocity is generated by applying a phase gradient between the same-frequency pumps feeding the devices, which play the role of the magnetic field in a Faraday medium. We incorporate these Josephson-based, nonreciprocal devices into a qubit

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[1] **NSTD Postdoc Finalist**

setup and demonstrate fast, high-fidelity, QND measurements of the qubit while actively protecting it against Josephson amplifier backaction.

10:00am **MP+EM+MN+NS-MoM6 Nonlinear Light-matter Interaction: From Superconducting Qubits to Spins in Diamond***, **Eyal Buks,*** Israel Institute of Technology, Israel

Cavity quantum electrodynamics (CQED) is the study of the interaction between matter and photons confined in a cavity. In the Jaynes-Cummings model the matter is described using the two-level approximation, and only a single cavity mode is taken into account. The interaction has a relatively large effect when the ratio $E/\hbar\omega$ between the energy gap E separating the two levels and the cavity mode photon energy $\hbar\omega$ is tuned close to unity.

The talk is devoted to the study of the light-matter interaction in the nonlinear regime using three different CQED systems. In the first experiment a Josephson flux qubit serves as a two-level system and a superconducting resonator as the cavity [1]. We experimentally find that the cavity response exhibits higher order resonances (called superharmonic resonances) in the nonlinear regime when the ratio $E/\hbar\omega$ is tuned close to an integer value larger than unity. In the second experiment the interaction between a spin ensemble of diphenylpicrylhydrazyl (DPPH) molecules and a superconducting resonator is explored in the region where $E/\hbar\omega \gg 1$ [2]. We find that the cavity response is significantly modified when the spins are intensively driven close to their Larmor frequency. Retardation in the response of the spin ensemble gives rise to effects such as cavity mode cooling and heating. In the third experiment the interaction between localized spins in diamond (nitrogen-vacancy and nitrogen substitutional) and a superconducting resonator is studied [3]. We find that nonlinearity imposes a fundamental limit upon sensitivity of CQED-based spin detection.

References

1. Eyal Buks, Chunqing Deng, Jean-Luc F.X. Orgazzi, Martin Otto and Adrian Lupascu, Phys. Rev. A 94, 033807 (2016).

2. Hui Wang, Sergei Masis, Roei Levi, Oleg Shtempluk and Eyal Buks, Phys. Rev. A 95, 053853 (2017).

3. Nir Alfasi, Sergei Masis, Roni Winik, Demitry Farfurnik, Oleg Shtempluck, Nir Bar-Gill and Eyal Buks, arXiv:1711.07760.

10:40am **MP+EM+MN+NS-MoM8 Variations in Surface Dipole-Moment Density with Coverage for C/Au(110) – (2 × 1) and Electroplated Au Ion-trap Electrodes***, **Dustin Hite,** K.S. McKay,* National Institute of Standards and Technology (NIST)*; H.Z. Jooya,* ITAMP, Harvard-Smithsonian Center for Astrophysics*; E. Kim,* University of Nevada, Las Vegas*; P.F. Weck,* Sandia National Laboratories*; H.R. Sadeghpour,* ITAMP, Harvard-Smithsonian Center for Astrophysics*; D.P. Pappas,* National Institute of Standards and Technology (NIST)

Ion traps, designed to test the feasibility of scalable quantum information processing, suffer from excessive electric-field noise that increases strongly as the ion-electrode spacing decreases in progressively smaller traps. This noise couples to the charge of the ions in the trap causing motional heating, which can result in the decoherence of quantum logic gates. This heating can be reduced by orders of magnitude with the use of cryogenic trap electrodes or by in-situ surface cleaning with ion bombardment in traps with room-temperature electrodes. Many experiments over the past two decades have supported theories that model this noise source as being caused by fluctuations in the dipole moments of contaminant adsorbates on the metallic trap electrode surfaces. Gold electrodes are often used to avoid oxidation and other contaminants, nevertheless a thin carbonaceous layer of approximately 3 monolayers (ML) develops on Au, even due to air exposure alone. In this work, we have studied the model system of C/Au(110) – (2 × 1) to understand the mechanisms for the variations in the surface dipole-moment density as a function of the degree of carbon coverage. We have implemented Kelvin probe force microscopy, along with x-ray photoelectron spectroscopy, to determine an average dipole-moment density with increasing carbon coverage, and have compared the results to density functional theory aided by ab-initio molecular dynamics techniques. We find a nearly linear decrease in the work function with a rate of approximately -0.7 eV/ML for sub-monolayer coverages, a regime in which trapped ions have been observed to have a maximum rate of heating. Finally, we compare the results for the model system to those for a microfabricated ion-trap chip with electroplated Au electrodes contaminated with a native hydrocarbon layer incrementally removed by ion bombardment.

11:00am **MP+EM+MN+NS-MoM9 A Compact Cryogenic Setup for Quantum Computing with Trapped Atomic Ions***, **Ismail Inlek**, R. Spivey, G. Vrijsen, Z. Jia, J. Kim,* Duke University

Trapped atomic ions are standard qubits for quantum computing with their long coherence times and high-fidelity qubit operations for universal quantum logic gates. However, conventional trapped ion systems often utilize bulky vacuum and optics setups, hindering scalability and ease of use. We aim to address these infrastructure issues by packaging micro-fabricated ion traps in an ultra-high vacuum (UHV) environment and designing optics to be an integral part of the overall system. Additionally, small footprint of the sealed UHV package allows users to easily install it on a cryostat to benefit from lower heating rates and further reduced vacuum levels. Moreover, these ion trap packages can be conveniently swapped to benefit from micro-fabricated ion trap manufacturing improvements without external UHV maintenance requirements. Towards achieving this goal, we report successful ion trapping in a compact cryogenic setup and characterize the performance of our apparatus for quantum computing applications.

11:20am **MP+EM+MN+NS-MoM10 Advances in Trapped Ion Quantum Computing***, **Jungsang Kim,*** Duke University **INVITED**

Trapped ions provide a highly desirable physical substrate on which to construct a scalable quantum computer. All qubits are exactly identical by nature, can be well isolated from the environment to establish long coherence times, and high fidelity quantum logic gates have been readily available. Furthermore, the long-range Coulomb interactions used for multi-qubit gates in a chain allows for highly connected network of qubits that are fully programmable, opening up opportunities for advanced and flexible quantum computer architectures. Some of the most advanced and complex quantum algorithms have been implemented in trapped ion systems leveraging these features. On the other hand, the ion trap systems so far have mainly relied upon conventional methodology used in atomic physics labs to set up the lasers, vacuum chambers and their optical alignments to realize the system. Novel integration technologies, including micro-fabrication, micro-electromechanical system (MEMS), and advanced packaging approaches have been adopted in the past decade to push the integration level for trapped ion systems. In this presentation, I will summarize the state-of-the-art systems used to implement quantum computing applications in the laboratories today, and also outline system design approach currently undertaken to improve the stability, reliability, and programmability of trapped ion quantum computers. Then, I will discuss the opportunities and challenges ahead for reaching a scalable quantum computer capable of executing useful tasks.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+2D+AN+EM+MN+MP+PC+RM-MoM

IoT Session: Nanostructured Devices and Sensors

Moderators: David Czaplewski, Argonne National Laboratory, Liya Yu, NIST Center for Nanoscale Science and Technology

8:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM1 Integrating Nanodiamonds with Augmented Artificial Intelligence and Digital Health to Optimize Combination Therapy***, **Dean Ho,*** UCLA **INVITED**

Dean Ho, Ph.D.

Nanodiamonds have emerged as promising candidates for clinical drug delivery due to their ability to carry a wide range of candidate therapies, unique surface properties, and biological tolerability. This lecture will highlight our recent clinical trial to validate a nanodiamond-embedded biomaterial for root canal therapy indications [1]. We will discuss the broad spectrum of efficacy, safety, characterization, and other studies that bridged in vitro with preclinical and downstream in-human studies. This lecture will also discuss upcoming clinical nanodiamond-based drug carrier studies, as well as our work in augmented artificial intelligence (AI) to develop globally optimized nanodiamond-modified therapy. Pairing nanodiamond platforms with augmented AI will lead to major advances in drug development and markedly improve response rates and treatment outcomes for a broad spectrum of disorders. Our recent clinical trials using these powerful combination therapy optimization technologies and digital health platforms to scale their implementation to usher in a new era of nanomedicine-based treatment will also be discussed [2].

1. Lee et al., Proceedings of the National Academy of Sciences, 2017

2. Zarrinpar et al., Science Translational Medicine, 2016

9:00am **NS+2D+AN+EM+MN+MP+PC+RM-MoM3 Morphology-Controlled Large-Scale Tin Oxide Nanostructures for Highly Sensitive Room Temperature Gas Sensor***, Amrit Sharma,* Norfolk State University

Highly sensitive large-scale tin oxide (SnO_2) nanostructures were grown on a glass substrate by vapor-liquid-solid (VLS) process using a mixture of anhydrous tin (II) chloride ($SnCl_2$) and zinc chloride ($ZnCl_2$) powders. We demonstrate a new kind of single cell vapor deposition system to precisely control nanostructural morphology by changing the weight ratio of $SnCl_2$ and $ZnCl_2$ and growth temperature. The morphology and structural property of as-grown nanostructures were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The SEM images revealed that the SnO_2 nanostructures with different densities, sizes, and shapes can be achieved by adjusting the weight ratio of $SnCl_2$ and $ZnCl_2$. SnO_2 nanostructures with diameter ~20 nm and length ~100 nm showed ~85% sensitivity and 53 seconds of response time, whereas the nanorods with diameter ~100 nm and length ~ 1mm showed ~50% sensitivity with 198 seconds response time. The nanostructured material with small size and shape showed better sensitivity on sensing at room temperature compared to previously reported SnO_2 based sensors.

9:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM4 Improving the Localized Surface Plasmonic Resonance Sensing Properties by Composite Metal/Dielectric Mixtures***, **Steven Larson**[1], Y. Zhao,* University of Georgia

Localized surface plasmon resonance (LSPR)-based sensors, whose resonance absorbance wavelength responds to the change in the local dielectric environment have attracted great attention and have been widely studied over the past decade. These sensors are traditionally improved by modifying the shape, size, and gap in the plasmonic nanostructure of the sensor. The sensitivity can also be tuned by the dielectric constant of the plasmonic material, such as noble metal alloys, but the improvements are not significant. Here we show that using a metal-dielectric composite, one can significantly improve the sensitivity of a LSPR sensor. Regular nanotriangle pattern samples composed of a mixture of Ag and MgF_2 with different composition ratios are prepared by combining nanosphere lithography and electron beam co-deposition. The plasmon resonance of these composite nanostructures at high Ag composition (C_{Ag})are shown to redshift with C_{Ag} until a composition threshold ($C_{Ag} \leq 90\%$) is met, where the resonance wavelength is nearly constant, slightly blue shifting. Multiple morphological and compositional characterization techniques are used to confirm that the shifts in the plasmonic properties are due to the change in composition and not a change in the morphology. The resulting LSPR sensor at C_{Ag} = 90 at.% can achieve a sensitivity of 696 RIU/nm, as compared to 312 RIU/nm for the same nanotriangle with pure Ag. This significantly improved sensitivity is due to the modified dispersion relationship of the dielectric constant by the composite and will play an important role in future plasmonic material design and applications.

9:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM5 Improving the Selectivity of Tin (IV) Oxide Paper Based Gas Sensors with Plasma Surface Modification***, **Kimberly Hiyoto**, E.R. Fisher,* Colorado State University

Metal oxide nanomaterials are desirable for solid-state gas sensors because of their ability to detect a wide variety of gases through changes in resistance resulting from gas-surface interactions. When optimizing these sensors, the supporting substrate is rarely considered, resulting in devices that are often brittle and have a fixed amount of nanomaterial that can be exposed to target analytes. Recent work using paper as the supporting substrate yields more affordable sensors that are flexible, allowing for a more robust device. Furthermore, the porous morphology of the paper also provides a larger surface area to attach metal oxides when compared to a traditional flat substrate of the same dimensions. Another limitation of these metal oxide sensors is inherent in the detection method. The lack of selectivity and required operating temperature of ≥300 °C limits the widespread use of metal oxide sensors. Dopants or the addition of a filter in the device design are typical approaches to address these problems; however, this increases fabrication complexity and cost. Plasma processing is a promising strategy to address these issues because it maintains desirable bulk properties but modifies the surface of the material to enhance gas sensor performance.

Here, we describe the Ar/O_2 plasma modification of paper based, tin (IV) oxide (SnO_2) nanoparticle devices as a function of applied rf power and precursor pressure. After plasma modification, the paper-based sensors exhibited improved response to carbon dioxide, ethanol, and benzene when compared to the untreated material on a more traditional substrate, zirconium dioxide. Additionally, sensor response to a target gas changed depending on the plasma modification parameters used, indicating the selectivity of these SnO_2 sensors can be easily tailored via plasma processing. Response and recovery studies of both the treated and untreated sensors will be discussed to demonstrate the dynamic behavior of these devices to the target gases as another measure of gas sensor performance and durability. Along with sensing behavior, optical emission spectroscopy and X-ray photoelectron spectroscopy provide insight into how the plasma modified the material, ultimately elucidating the relationship between material surface chemistry and sensor selectivity. Finally, preliminary work using this same fabrication process with another type of metal oxide gas sensor will be discussed to demonstrate the applicability of this method for other types of materials. Ultimately, these data work toward improved understanding of the gas sensing mechanism to design better performing gas sensors.

10:00am **NS+2D+AN+EM+MN+MP+PC+RM-MoM6 TiN@Si_3N_4 Core-shell Heterostructures as Nanoantennas for Photocatalytic Reforming of Methanol***, **Alejandro Alvarez Barragan**, L. Mangolini,* University of California, Riverside

The light-harvesting capacity of plasmonic nanoparticles has recently garnered attention in the synthesis of nanoantennas for photocatalysis. Aluminum, gold, and silver have been used to successfully drive hydrogen dissociation and CO oxidation reactions by injecting hot electrons into chemically active catalysts —such as platinum and palladium— adsorbed to their surface. However, the low response of aluminum at visible-near infrared (vis-NIR) wavelengths, the high cost of silver and gold, and the low thermal stability of these three metals, inspire the quest for alternative plasmonic materials that could potentially expand the field towards more ambitious and cost-effective applications. Titanium nitride (TiN) is a conductive ceramic with high hardness and bulk melting point (2930 °C). Its plasmon resonance located in the vis-NIR region, low cost relative to gold and silver, and well-understood properties as a thin film in the semiconductor industry, make it a strong alternative to mainstream plasmonic metals. The present work encompasses a comprehensive study of the oxidation kinetics of TiN particles at the nanoscale and an exploration of its role as nanoantennas for light-induced methanol reformation. TiN particles are synthesized via a scalable, modular, non-thermal plasma method. Titanium and nitrogen precursors are transported into a RF frequency plasma where TiN particles nucleate and grow. The high surface area and nitrogen deficiency of the particles facilitate the oxidation of the material and weaken its plasmonic response. The introduction of a secondary reactor with an input of SiH_4 as precursor gas leads to the formation of a Si_3N_4 coating. STEM and XPS analyses show that Si_3N_4 acts as a diffusion barrier, dramatically reducing the oxidation of the ~8 nm TiN particles. UV-vis-NIR spectrophotometry data show that the core-shell heterostructures experience a substantial blue-shift of the plasmon peak and an increase in intensity compared to the bare TiN. Platinum nanoparticles were subsequently deposited on the TiN@Si_3N_4 by photo-induced reduction of an aqueous solution of chlorplatinic acid. After rinsing and centrifuging, the Pt/TiN@Si_3N_4 heterostructures were diluted in a 50:50 water/methanol solution. Upon photoexcitation via white light illumination, hydrogen generation was readily detected by gas chromatography. This work also highlights the wide range of applications available for light-induced processes, ranging from materials processing (deposition of Pt particles) to photocatalysis (methanol reforming). It also strengthens the case for alternative plasmonic materials in a field dominated by precious metals.

10:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM8 Nanostructured Sensor and Device Applications of Infiltrated Zinc Oxide***, **Leonidas Ocola**,* Argonne National Laboratory*; Y. Wang, J. Chen,* University of Wisconsin-Milwaukee*; P. Blaisdell-Pijuan,* California State University-Fullerton*; R. Divan,* Argonne National Laboratory **INVITED**

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

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[1] **NSTD Student Award Finalist**

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

With the purpose of investigating quantum applications of infiltrated ZnO, we also have characterized the growth of ZnO in PS-b-PMMA block copolymers (BCP) of spherical and cylindrical sub-20 nm morphologies and studied how the photoluminescence of these nanostructures varies per its seed layer. We report blue-shifted photoemission at 335nm (3.70eV), suggesting quantum confinement effects. Samples of ZnO prepared with an alumina seed layer showed additional defect state photoemission at 470nm and 520nm for spherical and cylindrical BCP morphologies, respectively. Defect photoemission was not observed in samples prepared without a seed layer. No Raman peaks were observed for any samples with less than four cycles of ZnO, implying the absence of phonons and the functionality of these ZnO nanostructures as isolated emitters. To that effect we have demonstrated a fabrication path to isolate single infiltrated cylinders, paving the way for further studies of optical properties of individual 20 nm ZnO nanostructures.

- Use of the Center for Nanoscale Materials an Office of Science user facility, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

11:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM10 Templates for the Investigation of Size-Selected Nanocluster Networks***, **Patrick Edwards**, V.V. Kresin,* University of Southern California

The study of metal nanoclusters has revealed quantum nanoscale effects unique to the fully size-resolved regime. A highly notable example is electronic shell structure, akin to that in atoms and nuclei, which arises when confined conduction electrons organize into discrete energy levels. One consequence is the possibility of dramatic enhancement in electron Cooper pairing. Recent research from our group has provided evidence of this enhancement in certain free Al nanoclusters, with the electronic transition taking place at a temperature two orders of magnitude above that of bulk aluminum. We now aim to take advantage of this phenomenon by exploring the pairing transition in size-selected nanoclusters soft-landed on an appropriate substrate. Of particular interest are graphene and nanotube device architectures which provide unique templates for organizing nanocluster arrays. For example, a network of such superconducting nanoislands may induce superconductivity in graphene even at low coverages. Theory also predicts that an array of nanoclusters will not only support, but even enhance the Josephson current by 2-3 orders of magnitude. Carbon allotropes offer two distinct advantages for our system. First, the weak out-of-plane bonding provides a surface with less potential to disturb the structure of the soft-landed nanoclusters. Second, the tunability of graphene and carbon nanotube-based field effect transistors offers a versatile probe of nanocluster properties. We are also investigating the use of biological nanowires (bacterial flagella) as potential scaffolds upon which to deposit such nanocluster networks. These abundant and naturally occurring nanowires could serve as low cost and highly reproducible alternatives to the more common metallic or semiconductor templates.

Research supported by the Army Research Office (W911NF-17-1-0154).

11:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM11 High Performance Detection for X-ray and g -ray with $MAPbX_3$ Perovskite Single Crystals***, X. Wang, Z. Zhu, Q. Li, J. Wu, X. Zhang, B. Wang, **Wei Lei,*** Southeast University

Recently, organometallic lead trihalide perovskites have emerged as a new generation of opto-electronic materials. However, the high performance detection for x-ray and gamma-ray with $MAPbX_3$ is still a big challenge. For x-ray and gamma-ray detections, the detectors should have high sensitivity. If the photon counting method is adopted, the high energy resolution and high time resolution are also required. In this work, the large area $MAPbBr_3$ single crystal has been fabricated with a facile methodology. Due to the quite thick active material and large carrier mobility, the x-ray photons and gamma-ray photons can be absorbed with high efficiency. The photo generated electrons and holes can also be collected effectively with the large electric field. To decrease the dark current in the detection, a novel photo-diode structure is proposed here. In crystallization process of $MAPbI_3$ single crystal, the p-n junction can be formed with doping of selenium atoms into $MAPbI_3$ single crystal.

With various temperature method, the 30mm×30mm×7mm $MAPbBr_3$ single perovskite crystal is fabricated. As the experimental results shown, almost all of the 100 keV x-ray photons are absorbed when the $MAPbBr_3$ SPC is 7mm thick. The detection sensitivity is as high as 305 $\mu C\ Gy_{air}^{-1}cm^{-2}$when the anode voltage of x-ray tube is 30 kV .

To reduce the dark current in the detection, two type of photo diode structures have been proposed here. Firstly, a photo diode with structure of $Au/TPD/MAPbBr_3$ $PSC/C_{60}/PCBM/Ag$ has been fabricated with spin coating and sputtering methods. Although the dark current density can be reduced to 20 nA/cm^2 with -30V bias voltage, the temporal response time is nearly 50 µs due to the defects on the interfaces between PSC and carriers transport layers. Then, by doping selenium (Se) in $MAPbI_3$ perovskite single crystals (DPC) crystallization process, low dark current p-n junctions were fabricated without any organic layers. This photodiodes gives the high detection sensitivity as 21000 $mC\ Gy_{air}^{-1}cm^{-2}$ and 41 $mC\ Gy_{air}^{-1}cm^{-2}$ for 60 keV x-ray and 1.33 MeV gamma-ray respectively. In this photodiode, the transition time becomes shorter under higher electric field, and the carrier lifetime also becomes shorter due to the dopant of Se atoms. Finally, the temporal response time is measured as 3 µs by experiments. The FWHM width of energy spectrum is decreased to 3.2%@1330 keV.

Plasma Science and Technology Division
Room 104A - Session PS+AS+EM+SS-MoM

Plasma-Surface Interactions

Moderator: Yohei Ishii, Hitachi High Technologies America Inc.

8:20am **PS+AS+EM+SS-MoM1 Atomic-scale Numerical Simulation of a Nanometer-Scale Hole Etching of SiO2 with a Carbon Mask***, **Charisse Marie Cagomoc**, M. Isobe, S. Hamaguchi,* Osaka University, Japan

The current generation of mass-produced semiconductor devices uses nanometer-scale technologies to fit millions of transistors in a single chip. However, the demand for higher integration density is still increasing. For example, sub-10 nanometer transistors have been already established for experimental devices, and fabrication technologies of such devices for mass production are now being developed. For nanometer-scale fabrication processes, the granularity of the structure reflecting the finiteness of atomic sizes and the stochasticity of atomic motion may play important roles in determining the final structure. In this study, to understand such atomic-scale effects in nano-scale fabrication processes, we performed molecular dynamics (MD) simulations of etching processes for silicon dioxide (SiO_2) with a carbon mask having a 4-nm diameter hole by energetic fluorocarbon ions. The incident ion energy was typically in the range from 200eV to 1000eV. For example, in the case of CF_3+ ion injections, we observed that the depth of the etched out SiO_2 increased with increasing incident ion energy while the channel width became narrower as the etching of SiO_2 went deeper. Tapering of the carbon mask was also observed when the incident ions hit and deform the mask instead of going straight towards the SiO2. Furthermore, if the incident energy was too high (e.g., 1000 eV in this case), closing of the carbon mask hole occurred due to the formation of long carbon chains that moved across the hole and were bonded to the opposite side. Deposition of carbon atoms from the mask onto the sidewalls of the etched SiO_2 was also observed, which caused the formation of silicon carbide and may have impeded horizontal etching of SiO_2.

8:40am **PS+AS+EM+SS-MoM2 SF_6/O_2 Plasma Nanotexturing of Silicon: Decoupling How Ion Flux and Ion Energy Matter***, **Guillaume Fischer**[1],* Institut Photovoltaïque d'Ile-de-France (IPVF), France*; E. DRAHI, S.A. FILONOVICH,* Total SA Renewables, France*; E.V. Johnson,* LPICM, CNRS, Ecole polytechnique, Université Paris-Saclay, France

Crystalline silicon (c-Si) solar cell performance can be improved by reducing front surface reflectance. A drastic decrease may be obtained by texturing the surface at the nanoscale ("nanotexturing"), leading to a graded refractive index from air to c-Si. SF_6/O_2 plasma etching of c-Si in a capacitively coupled radiofrequency (CCP-RF) discharge is known to induce spontaneous nanotexturing. This phenomenon – typically resulting in the formation of conical nanostructures (NS) with typical sizes ranging from 30 to 500 nm – occurs through *in-situ* formation of non-volatile inhibitors on

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

the surface. The latter compete with simultaneous physical and chemical etching, and all these mechanisms may be influenced by ion bombardment.

In the present study, the ion energy distribution at the substrate electrode is tuned using Tailored Voltage Waveforms (TVWs) excitation in a reactive ion etching system. TVWs are obtained by adding harmonic frequencies with controlled amplitudes and phase-shifts to the basis driving signal at 13.56 MHz. This technique may give rise to amplitude and slope asymmetries in electronegative plasmas such as the SF_6/O_2 mixture.

Taking advantage of the edge-high total ion flux radial profile on the electrode but with a uniform energy distribution profile, we investigate the influence of both ion energy and ion flux on the nanotexturing process. Process conditions (etching time and driving voltage, i.e. sinusoidal signal or TVWs) are varied, and four samples are simultaneously textured for each set of conditions. The variations in etch rate suggest an ion energy-dependent etching yield. A phenomenological model (etching yield varying with the square root of the ion energy above a threshold at 13 eV) is proposed, and leads to the determination of a clear dependence between the energy weighted ion fluence and the final total hemispherical reflectance of the samples.

This trend is of great relevance for photovoltaic applications, and is explained by the constant increase in NS height during the process, which gradually smoothens the transition of refractive index from air to c-Si. However, the instantaneous ion flux is still observed to influence the aspect ratio (ratio between average height and width of the NS): the higher the ion flux, the higher the aspect ratio. This effect may stem from reduced lateral expansion of inhibitor species on the NS flanks due to the higher ion flux, and will affect the subsequent surface passivation required for photovoltaic applications. Finally, design rules for silicon nanotexturing using SF_6/O_2 plasma are drawn from the observed trends.

9:00am **PS+AS+EM+SS-MoM3 Corrosion Resistance to F and Cl plasma of Yttrium Oxyfluoride (YOF) formed by Sintering***, **Akinobu Teramoto**, Y. Shiba, T. Goto,* Tohoku University, Japan*; Y. Kishi,* Nippon Yttrium Co., Ltd, Japan*; S. Sugawa,* Tohoku University, Japan

Corrosion resistance to the reactive species in some kinds of plasma is very important to construct the reliable semiconductor process equipment. Especially the Fluorine and/or Chlorine plasma have the strong corrosiveness, and then it is strongly required that the inner wall material of the plasma chamber and the components in the plasma chamber have corrosion resistance to them. We have reported the Yttrium oxyfluoride (YOF, Y:O:F=1:1:1) film has the higher resistance to some plasma conditions (N_2/Ar, H_2/Ar, NH_3/Ar, NF_3/Ar, O_2/Ar) than the Y_2O_3 and YF_3 films [1, 2]. In this presentation, we report the corrosion resistance to NF_3/Ar, Cl_2/Ar and O_2/Ar plasma of YOF formed by sintering. The Y, O and F composition was controlled by mixing ratio of the YOF, YF_3, and $Y_5O_4F_7$ before the sintering, as the results, the O concentration was varied from 3 to 12 %. All YOF formed by the sintering are more stable to NF_3/Ar and O_2/Ar plasma than the YOF film and both Y_2O_3 film and formed by sintering. Cl_2/Ar plasma shows the stronger corrosion effect to the Y_2O_3 and YOF's, however the corrosion resistance to Cl plasma of YOF's is higher than the Y_2O_3.

These results indicate that the YOF is much stable against the corrosion by the plasma, and YOF formed by sintering is the promising material to construct the components in the plasma chamber.

Acknowledgement

The plasma irradiation and inspection were carried out in Fluctuation-Free-Facility in Tohoku University.

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9:20am **PS+AS+EM+SS-MoM4 Decay of Hydrogen in NF_3/Ar and O_2/Ar Cleaning Process by Optical Emission Spectroscopy***, **Hanyang Li**, Y. Zhou, V.M. Donnelly,* University of Houston*; J. Chiu, X. Chen,* MKS

Fluorine atom-generating plasmas are commonly used in many cleaning processes after chambers have been exposed to a variety of etching and deposition reactants and products. The most common feed gas used in these applications is NF_3, due mainly to its ease of dissociation. Repeated processing and chamber cleaning cycles can cause changes in the plasma source, thought to be due mainly to an altering of the nature of the chamber wall protective coatings. In the present study, high power density (5 – 50 W/cm^3), low frequency (400 kHz) toroidal inductive plasmas were operated with H_2/Ar (4/96) and N_2/H_2/Ar (3/9/88) feed gases for various periods, alternating with exposure to NF_3/Ar, O_2/Ar, or pure Ar "chamber cleaning" plasmas. H Balmer-alpha optical emission intensity, ratioed to emission from Ar at 750.4 nm, was measured during H_2/Ar exposure and the following cleaning plasma. Hydrogen was detected evolving from the anodized Al plasma source wall coating. The decay of intensity ratio of H/Ar increased with increasing H_2/Ar plasma exposure. NF_3/Ar plasmas enhanced evolution of H, tentatively ascribed to diffusion of F into anodized Al (most likely as F^-), which reacts with H that would otherwise remain trapped in the layer. The HF product then out-diffuses, leading to plasma dissociation and H emission. Conversely, O_2/Ar plasmas suppressed the evolution of H, presumably because O bonds to Al in anodized Al and ties up hydrogen as bound OH.

9:40am **PS+AS+EM+SS-MoM5 Plasma-surface Interactions in the Strongly Coupled Regime***, **Thomas Morgan**,* DIFFER, Netherlands **INVITED**

At high fluxes and densities the interaction of a plasma with the walls of its confinement enter the strongly coupled regime [1], where the mean free paths for collisional processes become much smaller than those of the plasma scale size. The surface morphology in such cases may be pushed far out of equilibrium and in turn the recycling and erosion strongly perturbs the near-surface plasma. Such conditions are reached in high flux plasma processing as well as the exhaust region of future large-scale fusion reactors such as ITER and DEMO. The linear plasma generator Magnum-PSI [2] is uniquely capable of achieving high density low temperature plasmas with high similarity to fusion reactor exhaust fluxes. Using this device the power handling, long term erosion and evolution of plasma facing materials for ITER and DEMO can be studied, as well as the self-organisation effects and novel structures which occur under such conditions. At plasma-liquid metal interfaces considered as advanced wall components this strong coupling can give rise to vapour shielding of the surface, indicating a novel method to limit heat loading damage to wall surfaces in the reactor exhaust [3]. An overview of results will be given showing how this device is addressing urgent questions for ITER, helping to develop advanced walls for DEMO and beyond, and exploiting non-equilibrium for plasma processing.

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10:40am **PS+AS+EM+SS-MoM8 Tailoring the Surface Properties of Porous Zeolite Constructs using Plasma Processing***, **Angela Hanna**[1], E.R. Fisher,* Colorado State University

Zeolites have been widely used for adsorption, catalysis, and gas separation processes. Despite their extensive use, the ability to control the surface properties of zeolites remains unoptimized. Plasma modification presents an ideal modification methodology with a wide parameter range and the potential to create tailored surface properties and functionalities. Thus, we sought to improve material performance through plasma surface modification, as well as through fabrication of various zeolite constructs (i.e., native zeolites, pellets and electrospun fibers). Moreover, our approach to understand the fundamental plasma chemistry allows us to provide significant insight into mechanisms that will ultimately provide a more thorough evaluation of plasma processing for zeolite surface modification. We employed a range of characterization tools to assess materials before and after plasma treatment and optical spectroscopies to examine the gas-phase of the plasma, both with and without zeolites to evaluate the impact of the material on the gas-phase. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy, and powder X-ray diffraction were utilized to assess surface chemistry, substrate morphology, and bulk characteristics of the material, respectively, before and after plasma exposure. Water contact goniometry was employed to evaluate the surface wettability, where untreated zeolites were nominally hydrophilic. Here, we explored two fluorocarbon (FC) precursors (i.e., C_2F_6 and C_3F_8) to create more hydrophobic surfaces than the untreated materials. XPS analysis reveals surface fluorination and/or formation of a FC coating on the material. $H_2O_{(v)}$ plasmas were also employed to create a more hydrophilic zeolite surface, while maintaining a porous, interconnected network. By also studying the gas-phase, we can glean how the material changes the plasma environment. Species interactions and plasma energetics are intertwined; thus, temporally-resolved data are necessary to accurately probe the intricate dynamics within plasmas. We have investigated formation and destruction mechanisms of key excited state species (i.e., CF, CF_2, OH) to provide mechanistic insight that could be

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[1] **National Student Award Finalist**

correlated with system energetics data and material properties. Emission spectroscopy was also used to measure the relative gas phase densities of the aforementioned key species as a function of plasma operating parameters (i.e., power, gas mixture, substrate architecture). Our studies have revealed correlations between gas-phase spectroscopic analyses, the gas-surface interface, and the resulting plasma modified surface properties, ultimately leading to improved plasma processes.

11:00am **PS+AS+EM+SS-MoM9 Generation Kinetics of Plasma-induced Electronic Defects in Semiconductor Materials***, **Shota Nunomura**, I. Sakata, K. Matsubara,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

In state-of-the art semiconductor devices, electronic defects strongly influence the device performance. The electronic defects are often generated during the device fabrication, where a variety of plasma processing technology is used for film deposition, gate etching, dopant implantation and so on. Most defects are recovered by post-annealing, however some defects remain in the devices. Because these defects usually deteriorate the device performance, reduction of these defects is required. However, the kinetics of generation and annihilation of the defects are not fully understood yet.

We studied the kinetics of electronic defects in hydrogenated amorphous silicon (a-Si:H) during H_2 and Ar plasma treatments. The generation and annihilation of defects are monitored via in-situ photocurrent measurement during the treatment [1-2]. A decrease in the photocurrent indicates the generation of defects whereas an increase in the photocurrent indicates the annihilation of defects. This photocurrent-based monitoring is highly sensitive in the detection of small amount of defect density (~10^{16}cm^{-3}).

The photocurrents in a-Si:H films under various conditions of H_2 and Ar plasma were measured. From the measurements, we find the following [3]. (i) Each plasma treatment immediately causes the generation of defects, indicated by a strong reduction in the photocurrent. (ii) The defects are generated dominantly by the radicals such as hydrogen atoms (H) and argon metastable atoms (Ar^*). (iii) The residual defects are created by the bombardment of Ar^+ ions rather than H_3^+ ions, radicals and photons. However, the residual defects are recovered mostly by an additional H_2 plasma and post-annealing treatment. (iv) The radicals and photons also generates defects, however these defects are annihilated by the simple post-annealing. The details of the experimental setup, results and discussion are given in the presentation.

This work was supported by JSPS KAKENHI (Grant Number 18K03603 and 15K04717) and NEDO.

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11:20am **PS+AS+EM+SS-MoM10 Evolution of Photoresist Layer Structure and Surface Morphology under Fluorocarbon-Based Plasma Exposure***,* ***Adam Pranda****, S.A. Gutierrez Razo, J.T. Fourkas, G.S. Oehrlein,* University of Maryland, College Park

Fluorocarbon-based plasma chemistry is an integral component in enabling the pattern transfer step in the semiconductor manufacturing process. Although significant work has gone towards understand the overall etching behavior, surface roughness, and chemistry development for continuous-wave (CW) plasmas with Ar/fluorocarbon admixtures,[1] a complete understanding of the photoresist layer structure evolution and surface roughness distribution has not been well established. Specifically, under high-energy ion bombardment, a dense amorphous carbon (DAC) layer forms at the surface, impacting the etch resistance and surface roughness. For discrete evaluation of the DAC layer/fluorocarbon interaction, we employed a pulsed plasma setup in which a biased, steady-state Ar plasma was used to develop DAC layers of various thicknesses at the photoresist surface, after which fluorocarbon (C_4F_8) pulses of various lengths were introduced. We sought to answer three key questions: 1. How does the fluorocarbon interaction with the DAC layer impact the layer structure? 2. How is the surface roughness affected by the fluorocarbon interaction? 3. How does the pulsed process compare to a CW Ar/C_4F_8 admixture process?

For sample characterization, we utilized a combination of real-time, *in situ* ellipsometry and X-ray photoelectron spectroscopy at various points during the plasma exposure on an industry-standard 193 nm photoresist, several model polymers, and a 3-color-lithography-compatible photoresist that we are developing. Atomic force microscopy (AFM) was used to monitor the surface roughness evolution and the distribution was calculated using a power spectral density (PSD) analysis.

From the combined analyses, we find that the fluorocarbon depletes the DAC layer by a partial conversion of the surface of the DAC layer into an F-rich mixed layer. Furthermore, the mixing of the fluorocarbon into the DAC layer results in an overall smoothening of the sample surface. By comparing the pulsed process to the CW process, we evaluate the significance of the layer structure in determining the surface behavior in response to variations in fundamental plasma parameters such as the ion energy or exposure time.

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

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11:40am **PS+AS+EM+SS-MoM11 Fundamental Studies of Plasma Species with Organic Materials of Varying Hydrogen and Oxygen Composition by Computational and Experimental Approaches***,* ***Yusuke Fukunaga,*** Nagoya University, Japan*; P.L.G. Ventzek, B. Lane,* Tokyo Electron America, Inc.*; A. Ranjan,* TEL Technology Center America, LLC*; M. Sekine, T. Tsutsumi, H. Kondo, K. Ishikawa,* Plasma Nanotechnology Research Center, Japan*; R. Upadhyay,* Esgee Technologies*; L. L. Raja,* The University of Texas at Austin*; G. Hartmann,* McKetta Department of Chemical Engineering, The University of Texas at Austin*; G. S. Hwang,* The University of Texas at Austin*; M. Hori,* Institute of innovation for future society, Japan

Organic film etching is important for semiconductor device fabrication especially as it relates to self-aligned-multiple-patterning in which sub-nanometer scale pattern replication is critical. Even though the etching of organic materials has been studied for decades (e.g., O_2 plasma ashing), new process applications (e.g. ALE) and new chemistry regimes render older models of organic etching such as those employing the Ohnishi parameter of limited use.[1] Existing kinetic models rely on untested assumptions such as the role of dangling bonds as reaction initiating sites.[2] A need exists to revisit the fundamentals of plasma surface interactions as they pertain to the etching of organic films. Moreover, a need exists to incorporate fundamental kinetic models with macroscale models which could be used for process development.

Progress has been slow because of the computational weight of modeling the chemical kinetics and difficulty defining a tractable problem. In this presentation, we describe the use of an integrated modeling framework involving fundamentals-based ab-initio and plasma chemistry simulations with high performance computing to describe chemical kinetics on model polymer systems. In O_2 and Ar plasmas, we use finite carbon size strands with varying degrees of O, OH or H termination as model structures. For simplicity, the structures are polyethylene-like. We use density functional theory (DFT) to model the interactions between plasma species and representative structures. To estimate the relative importance of plasma species and their energy, we derive species and energy flux from a macroscale plasma chemistry model. Both DFT and ab-initio molecular dynamics (AIMD) simulations are used to probe the chemical stability of representative structures to different plasma species (e.g., Ar, O) and energy fluxes. We found that O addition to H terminated structures results in OH group formation on polyethylene by exothermic reaction. Ar ion bombardment formed carbon strands may also be oxidized. The resultant structures (oxo-carbon) are also stable up to large oxygen to carbon ratios. The stability to Ar ion bombardment will be presented. An essential test of any new mechanism is experimental validation. In addition to the computational results, we will present experimental results ranging from basic etch rate measurements to measurements of plasma processed material chemical composition (e.g., XPS).[3]

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Plasma Science and Technology Division
Room 104C - Session PS+TF-MoM

Plasma Deposition and Plasma-Enhanced ALD

Moderators: Kazunori Koga, Kyushu University, Japan, Erwine Pargon, LTM, Univ. Grenoble Alpes, CEA-LETI, France

8:20am **PS+TF-MoM1 ZrO_2 Deposition using a 2.45 GHz Atmospheric Pressure Plasma Torch**, ***Dhruval Patel**, L. Bonova, C. Ahn, D.V. Krogstad, D.N. Ruzic,* University of Illinois at Urbana-Champaign; *S. Chaudhuri,* University of Illinois at Chicago

Partially stabilized zirconia is widely used in thermal barrier coatings that requires a thermodynamically stable and highly durable interface with a natively grown aluminum oxide (Al_2O_3) scale. The potential of ZrO-$_2$ to serve as an effective Thermal barrier coating (TBC) has already been demonstrated along with modest corrosion resistance. The ECAP experiment (Evaporative Coatings at Atmosphere Pressure) was developed at CPMI (Center for Plasma Materials Interaction at UIUC) as a device for surface treatment at atmosphere pressure utilizing a 2.45 GHz microwave plasma torch. Recent modifications to this system allows for delivery of precursors and target materials through the torch that gives it the capability to deposit thin films. The goal of this study is to compare the quality of the ZrO-$_2$ films grown using each of these methods. Various methods will be used to characterize the quality of films grown including Nanoindentation, XPS, XRD and Profilometry.

8:40am **PS+TF-MoM2 Ion Energy Characteristics during Plasma-Enhanced Atomic Layer Deposition and their Role in Tailoring Material Properties**, ***Tahsin Faraz***[1], *K. Arts, S. Karwal, M.C. Creatore,* Eindhoven University of Technology, The Netherlands; *H.C.M. Knoops,* Oxford Instruments, The Netherlands; *W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

As we enter an era of atomic scale device dimensions, there is a significant demand for synthesizing ultrathin films with precise growth control. Plasma-enhanced atomic layer deposition (PEALD) has obtained a prominent position in obtaining films with atomic scale precision. Although the effects of ion-surface interactions have been investigated for conventional plasma-enhanced chemical and physical vapor deposition in great detail, very little is known about the role of ions during PEALD. In this work, we demonstrate how the properties of materials (oxides and nitrides of Ti, Hf and Si) grown using PEALD (on planar and 3D substrates) can be tailored by controlling the kinetic energy of ions, E_i, impinging on a growing film surface with RF substrate biasing.[1] This technique harnesses the well-known synergism of ion-radical processes under energetic ion bombardment during reactive plasma exposure. It was demonstrated to significantly enhance the versatility of PEALD processes by providing two knobs (magnitude and duration of bias) enabling control over materials with dielectric or conductive properties, relevant for a wide variety of applications.

We measured E_i characteristics of reactive plasmas typically used for PEALD (O_2, H_2, N_2) to investigate their role in tailoring material properties. Performing such measurements is essential towards understanding how a given PEALD process at different operating conditions can be influenced by energetic ions. Ion energy distributions (IEDs) were measured in a commercial 200-mm remote inductively-coupled-plasma (ICP) ALD system equipped with RF substrate biasing. IEDs were obtained using a gridded retarding field energy analyzer (RFEA) for the aforementioned plasmas without and with RF biasing. The properties of materials grown using these plasmas in this ALD system were analyzed as a function of the parameters derived from IEDs. These results have provided more insight on the relation between ion characteristics and the ensuing properties, e.g., identifying E_i thresholds between property improvement and degradation. They demonstrate how the measurement and control of E_i characteristics during PEALD provides a platform for synthesizing ultrathin films with desired properties.

Furthermore, we analyzed the effects of controlling E_i during PEALD on 3D substrates frequently employed in state-of-the-art devices. It yielded an intriguing effect of inducing differing material properties at different surfaces of 3D trench nanostructures. This demonstrated the potential of this technique in enabling new routes for achieving topographically selective deposition.

[1] Faraz *et al. ACS Appl. Mater. Interfaces* **10**, 13158 (2018)

9:00am **PS+TF-MoM3 Plasma Deposition of Functional, Nanostructured Coatings on Materials and Nanomaterials Derived from the Wood Biomass**, ***Luc Stafford**,* Université de Montréal, Canada **INVITED**

Wood components have been used as a building material for centuries. In light of the growing concern over the environmental impact of human industrial activity, wood has taken on a new importance worldwide. The main advantages of this widely-distributed and renewable resource lie in its versatility, strength-to-weight characteristics, ease of processing, aesthetics, and its sustainability as a green-material. Its bio-polymeric structure, however, renders it susceptible to degradation due to moisture, microorganisms, insects, fire, and ultraviolet radiation. In this context, important research efforts have been devoted to the further development of existing wood protection systems either through the application of paints, varnishes, stains, and water repellents or through direct modification by thermal, chemical, and impregnation methods. In recent years, we have shown that non-thermal plasmas represent a very promising approach for tailoring the surface properties of wood-based materials for both improvement of existing protection systems or as standalone treatment for the growth of functional coatings. In this presentation, the scientific and technological accomplishments associated with the use of plane-to-plane dielectric barrier discharges at atmospheric pressure for plasma-enhanced chemical vapor deposition (PECVD) of various barrier coatings on wood surfaces are reviewed. These aspects cover the effects of wood conditions and properties, such as wood inhomogeneities and wood outgassing, on both the plasma characteristics and the plasma deposition dynamics of SiOCH barrier layers using organosilicon precursors. This description is extended to more complex systems such as the plasma-assisted growth of nanocomposite coatings (for example TiO2 or ZnO nanoparticles embedded into a SiOCH matrix) using colloidal solutions as the growth precursor for PECVD. For such applications, a combined low-frequency-high-frequency voltage waveform is used to achieve significant and spatially uniform deposition of nanoparticles across the whole substrate surface. Finally, very recent studies on the plasma-assisted functionalization of highly porous microfibrillated cellulose materials derived from the wood biomass are presented.

9:40am **PS+TF-MoM5 Mechanisms of Halogenated Silane Decomposition on an N-rich Surface during Atomic Layer Deposition of Silicon Nitride**, ***Gregory Hartmann**,* University of Texas at Austin; *P.L.G. Ventzek,* Tokyo Electron America, Inc.; *K. Ishibashi, T. Iwao,* Tokyo Electron Technology Solutions Ltd., Japan; *G.S. Hwang,* University of Texas at Austin

Atomic layer deposition (ALD) has recently received increasing attention for the growth of high-conformity silicon nitride (SiN) thin films for use in microelectronics, particularly as charge storage layers in vertical-NAND. Plasma enhanced ALD (PEALD) allows SiN deposition at substantially lower temperatures (< 400 °C) with better film properties, compared to thermal ALD. The challenge of PEALD is that Si deposition must occur via a thermal mechanism due to the low temperatures. The PEALD of SiN films involves a two-step cycle: (1) adsorption and decomposition of silicon-containing precursors and ii) nitridation of the Si-rich surface by active N species emanating from the plasma. Halogenated silanes such as hexachlorodisilane, bis(tertiary-butyl-amino)- silane, and dicholorosilane (DCS, SiH_2Cl_2) have been utilized as Si precursors. Despite efforts directed towards process development, the underlying reaction mechanisms of Si deposition remain uncertain. Methods to improve growth rate and uniformity have been demonstrated experimentally, but without knowledge of the reaction mechanisms, direct contributions of specific process conditions cannot be explained. Using first-principles density functional theory (DFT) calculations, we have examined and identified a novel mechanism for the adsorption and decomposition of DCS on a N-rich SiN surface. Our study predicts that the DCS adsorption and dissociation can occur by overcoming a moderate barrier (» 0.3 eV), lower than the prohibitively large barriers predicted for previously proposed mechanisms. Through a detailed electronic structure analysis of the reaction intermediates, we have also elucidated the principles underlying the reaction mechanism, notably the hypercoordination of Si which permits the facile reaction of molecularly adsorbed DCS with primary and secondary amines on the surface, followed by dissociation releasing protons and Cl anions with subsequent HCl formation. We have examined the same mechanism utilizing alternative precursors and the predicted trends are found to be corroborated with the important properties of the system. Understanding these principles allows us to develop guidelines for processing conditions, such as the importance of maintaining the proper surface composition to facilitate Si precursor adsorption and dissociation.

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

Our study provides insight into the SiN ALD process via chlorosilanes and guidelines to control the deposition for high-quality SiN films and provides a framework for future theoretical studies of surface reactions during ALD.

10:00am **PS+TF-MoM6 Characterization of Inductively Coupled Plasma Source for Plasma Enhanced Atomic Layer Deposition***, **Premkumar Panneerchelvam**, A. Agarwal,* KLA-Tencor*; D.R. Boris, S.G. Walton,* Naval Research Laboratory

Plasma enhanced atomic layer deposition (PEALD) is a technique which provides an efficient alternative to thermal ALD systems by enabling low-temperature wafer processing using energetic and reactive plasma species. Utilization of plasma sources to drive atomic layer deposition stems from the ability to generate active radicals which are more reactive than molecular precursors used in thermal ALD processes. Aside from the fact that plasma processing systems are already utilized in semiconductor manufacturing, PEALD affords significant advantages over thermal ALD processing such as lower temperature processing coupled with active tuning of film properties, wafer level uniformity control, wider variety of film growth, and conformality. Remote inductively coupled plasma (ICP) sources are a common choice for PEALD as they enable high density discharges which efficiently generate reactive neutral species. Characterization of these plasma sources is important in understanding the properties of the species incident on the wafer to not only tailor the chamber architecture but also understand the role of different radicals in the plasma in the surface mechanism.

In this work, we will discuss characterization of a reactor that imitates an industrial PEALD tool using experimental and computational investigations. The system is flowing afterglow geometry, where a barrel-type ICP source is mounted on one side of the reactor and produces a plasma that expands into a chamber with access ports to diagnose the plasma properties using optical emission spectroscopy and charged particle flux probes. The computational model is based on a multi-species, two-temperature fluid description of plasma with finite rate chemistry. Results will be discussed in Ar and Ar/N$_2$ plasmas over varying pressure and inductive power with particular emphasis on the impact of N$_2$ addition on plasma properties and the chemical composition of radicals incident on the wafer.

*This work was partially supported by the Naval Research Laboratory base program.

10:40am **PS+TF-MoM8 Structural, Optical, and Electrical Properties of Plasma-Enhanced Atomic Layer Deposited ZnO: Influence of Substrate Temperature***, **Julian Pilz**, A. Perrotta, A.M. Coclite,* Graz University of Technology, Austria

ZnO is a direct band gap semiconductor with attractive piezoelectrical, optical, and electrical properties, particularly appealing for a variety of functional devices (e.g., gas, bio, and UV sensors, piezoelectric nanogenerators and actuators). Being able to tailor these material properties to meet specific technological requirements is crucial for enhancing the device efficiency or sensitivity.

In a previous study [1], the effect of plasma power on plasma-enhanced atomic layer deposited (PE-ALD) ZnO had been investigated at room temperature. By tuning the power, properties such as the refractive index, bandgap, and crystallite size had been tailored. However, the power had shown little influence on the texture of the crystalline films.

In this study, we investigated the effect of substrate temperature in the range 25 °C – 250 °C on the ZnO material properties. The films were grown by direct PE-ALD adapting diethylzinc and O$_2$-plasma as reactants. By adjusting the substrate temperature, it was possible to switch the texture of the films from (100) at room temperature to (002) above 150 °C. The growth per cycle (obtained by spectroscopic ellipsometry, SE) ranged from 1.6 to 4.0 Å/cycle, suggesting a temperature dependent growth behavior. Further SE analysis showed a range of refractive index (at 633 nm) from 1.87 to 1.94 and a bandgap range of 3.255 to 3.270 eV. X-ray photoelectron spectroscopy survey scans pointed out a non-detectable carbon content and a O/Zn ratio of around 1.17 (constant over the whole temperature range), while high-resolution scans of the O1s-peak showed a decrease in OH-content from 21 % (at 25 °C) to 9 % (at 250 °C). Further analysis will focus on resistivity (and its relation to OH-content), transparency, and piezoresponse.

Correlating the results of these techniques, interesting insights can be gained into the quality of the PE-ALD ZnO and which substrate temperature should be chosen for specific applications. This paves the way for optical, electrical, or sensing devices on the basis of tailored ZnO thin films, which can be grown conformally and with Å-level thickness control due to the PE-ALD characteristics.

[1] Pilz et al. "Tuning of material properties of ZnO thin films grown by plasma-enhanced atomic layer deposition at room temperature." J. Vac. Sci. Technol. A 36.1 (2018): 01A109.

11:00am **PS+TF-MoM9 Critical Effect of the Presence and Position of Double Bonds in the Atmospheric Plasma Synthesis of Organic Coatings***, **Jérémy Mertens**[1], J. Baneton, A. Ozkan, F. Reniers,* Université Libre de Bruxelles, Belgium

Last decades, atmospheric plasma systems have become a powerful tool for the synthesis of organic/inorganic coatings. Even though the well-known Yasuda parameter[1] is a good indicator of the fragmentation process of the injected monomers during the low-pressure synthesis, it faces severe limitations at ambient conditions. This can essentially be related to the wider range of collisions and the lower mean free path of the plasma species at atmospheric pressure. Also, the key role of the chemical structure of the injected monomer such as the presence of double bonds on the synthesized coating properties has not been included in the Yasuda model but strongly influences the plasma polymerization/fragmentation mechanisms.[2]

It is well known, not only in plasma science, that the presence of double bonds increases the deposition rate which has been confirmed in this research. Yet, our group previously demonstrated that unsaturations could also play a protective role of an ester function during the atmospheric plasma polymerization process[3] but no explanationwas proposed so far. Using various saturated and unsaturated precursors, this study proposes a novel point of view of the essential role of the presence of sp^2 carbon atoms, their spacing with a function of interest and the planar geometry of the monomer in the polymerization mechanisms in dielectric barrier systems. Therefore, the plasma phase and physico-chemical properties of the synthesized coatings analysis are correlated. The influence of the addition of each molecule on the electrical behavior of the discharge is monitored by oscilloscope measurements. The fragmentation of the precursor in the plasma, evidenced by in situ mass spectrometry and optical emission spectroscopy, show that the polymerization mechanisms are different when the precursor contains double bonds. The suggested synthesis pathways for each precursor are correlated to the surface and bulk chemical structure of the synthesized films, determined by X-Ray photoelectron spectroscopy and infrared reflectance absorbance spectroscopy. It is evidenced that the distance separating the function of interest from the double bond is a major parameter to take in account for the conservation of the structure of the injected molecule. We suggest that it is possibly due to a planar geometry arrangement and to a resonance phenomenon for specific double bonds positions.

The authors would like to thank the Walloon Region for their financial support through the FLYCOAT project (n°131847).

[1] H.K.Yasuda & al. , J. Polym. Sci., 16, 743

[2] J.Hubert & al., Plasma Process. Polym. **2015**, 12, 1174

[3] A.Batan & al., Plasma Process. Polym. **2013**, 10, 857

11:20am **PS+TF-MoM10 Capacitively Coupled DC/RF Discharges for PEALD Process of Titanium Dioxide Films***, **Shinya Iwashita**, A. Suzuki, T. Shindo, T. Kikuchi, T. Matsudo, Y. Morita, T. Moriya,* Tokyo Electron Technology Solutions Ltd., Japan*; A. Uedono,* University of Tsukuba, Japan

We are working on the development of a discharge source using tailored waveforms for plasma enhanced atomic layer deposition (PEALD) processes. The discharge sources employed in this study are 13.56 MHz RF, pulsed DC or their combination [1], and their applicability to PEALD process of titanium dioxide (TiO$_2$) thin films has been evaluated. A titanium precursor adsorbed on a silicon substrate having amorphous carbon (a-C) patterns is oxidized by applying these discharges in argon/oxygen mixtures. Thus PEALD process of TiO$_2$ films is achieved accordingly. The experimental results obtained from scanning transmission electron microscope show that TiO$_2$ films are deposited with excellent step coverage independent of the discharge sources. However, the film characteristics at each deposition position of a-C patterns (i.e. at the top, side and bottom) greatly vary depending on the discharge sources, which has been confirmed by the evaluation of the wet etching rate using a diluted hydrogen fluoride solution. The clear variation of the film characteristics is presumably attributed to the change in the number density of reactive species

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

(electrons, ions, radicals), their ratio and the ion angle distributions, all of which are determined by the discharge sources.

[1] Denpoh K and Ventzek P, *J. Vac. Sci. Technol. A* **26** (2008) 1415, Kawamura E et al *J. Vac. Sci. Technol. A* **25** (2007) 1456.

11:40am **PS+TF-MoM11 The Effects of Varying Plasma Conditions on Plasma Enhanced Atomic Layer Epitaxy***, D.R. Boris, V.D. Wheeler,* U.S. Naval Research Laboratory*; V.R. Anderson,* Kennesaw State University*; N. Nepal,* U.S. Naval Research Laboratory*; S.G. Rosenberg, A.C. Kozen,* ASEE Postdoctoral Fellow*; S.G. Walton,* U.S. Naval Research Laboratory*; **Charles R. Eddy, Jr.**,* U. S. Naval Research Laboratory

Plasma enhanced atomic layer epitaxy (PEALE) is a method for growing very thin crystalline films at low temperature in a conformal layer-by-layer manner that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas phase chemistry to produce varying film characteristics. The flexibility and lower growth temperatures that plasmas provide come at the cost of a complex array of process variables that often require great care on the part of the user.In response to this challenge, this work focuses on the use of plasma diagnostics to inform the choice of process conditions for PEALE systems. In this work we employ VUV-NIR spectroscopy and charged particle collectors to characterize the inductively coupled plasma source of a Fiji 200 (Ultratech/CNT) ALD tool. In particular, we assess the total ion flux reaching the substrate surface and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow fractions in context of PEALE of AlN, InN, TiO_2 and Ga_2O_3 films. Changes in plasma parameters are then linked with changes in film characteristics.________________________________* This work supported by the Naval Research Laboratory Base Program

Advanced Surface Engineering Division
Room 202C - Session SE+NS+TF-MoM

Nanostructured Thin Films and Coatings

Moderators: Jianliang Lin, Southwest Research Institute, Matjaz Panjan, Jozef Stefan Institute, Slovenia

8:20am **SE+NS+TF-MoM1 The Role of Mechanical and Chemical Bonding Mechanisms in Adhesion of Nanoporous Anodic Aluminium Oxides (AAO)***, **Shoshan Abrahami**,* Vrije Universiteit Brussel (VUB), Belgium*; V.C. Gudla,* Technical University of Denmark*; K. Marcoen,* Vrije Universiteit Brussel, Belgium*; J.M.M. de Kok,* Fokker Aerostructres*; T. Hauffman,* Vrije Universiteit Brussel, Belgium*; R. Ambat,* Technical University of Denmark*; J.M.C. Mol,* Technical University Delft, Netherlands*; H. Terryn,* Vrije Universiteit Brussel, Belgium

Anodic aluminum oxides (AAOs) are important nanostructures in many engineering applications. But despite their popular use, the important parameters that control their (dis-)bonding to an organic coating are not fully understood. This study uses an original approach that employs porous- and barrier AAO specimens for both chemical characterization and mechanical tests, thereby enabling the distinction between chemical and morphological contributions to the surface affinity for interfacial bonding. A validation for the cooperative effect of mechanical and chemical bonding mechanisms is given in this study. This was achieved by post-anodizing immersion of AAO's in sodium fluoride solution after anodizing in sulfuric acid (SAA) or a mixture of phosphoric- and sulfuric acid (PSA). Transmission electron microscopy (TEM) cross-section images show that fluoride-assisted dissolution smoothed the oxide surface, removing the fibril-like top nanostructure of the porous oxides, which are important for dry adhesion. However, chemical surface modifications were dependent on the initial oxide composition, as measured by X-ray photoelectron spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Chemical analysis reveals that the surface hydroxyls of AAO are partially replaced by fluorides that do not form interfacial bonding with the epoxy resin. As a result, the peel strength of SAA under wet conditions is severely reduced due to these chemical changes. Conversely, fluoride-assisted dissolution of surface phosphates in PSA compensates for the adsorbed fluorides and the wet peel strength of PSA panels is not further deteriorated.

[1] S.T. Abrahami et al., J. Phys. Chem. C, 119, 19967-19975 (2015).

[2] S.T. Abrahami et al., npj Materials Degradation, 1, 8 (2017).

[3] S.T. Abrahami et al., J. Phys. Chem. C, 120, 19670-19677 (2016).

9:00am **SE+NS+TF-MoM3 Two-dimensional Hexagonal Boron Nitride (hBN) Layer Promoted Growth of Highly-oriented, Trigonal-structured $Ta_2C(0001)$ Thin Films via Ultra-high Vacuum Sputter-deposition on $Al_2O_3(0001)$***, **Koichi Tanaka**, P. Arias, M.E. Liao, Y. Wang, H. Zaid, A. Aleman, M.S. Goorsky, S. Kodambaka,* University of California, Los Angeles

It is generally believed that single-crystalline substrates with either the bulk or surface structure and lattice constant identical or similar to that of the film being deposited are required for the growth of high-quality crystalline thin films. Recent studies have shown that deposition on van der Waals (vdW) layers can lead to highly-oriented thin films of a variety of crystal structures and lattice parameters. Here, we show that two-dimensional (2D) hexagonal boron nitride (hBN) layers (a = 0.250 nm and c = 0.667 nm) improve the crystallinity of trigonal-structured Ta_2C (a = 0.310 nm and c = 0.494 nm) thin films sputter-deposited on $Al_2O_3(0001)$ substrates. Ta_2C layers of desired thickness (t = 17 ~ 75 nm) are grown on bare and hBN-covered $Al_2O_3(0001)$ substrates via ultra-high vacuum direct current magnetron sputtering of TaC compound target in 20 mTorr pure Ar gas atmospheres at 1327 K. hBN layers are deposited via pyrolytic cracking of borazine (~600 L) onto $Al_2O_3(0001)$ substrates at 1327 K. The as-deposited Ta_2C films are characterized *in situ* using Auger electron spectroscopy and low-energy electron diffraction and *ex situ* using X-ray diffraction (XRD) and transmission electron microscopy (TEM) based techniques. ω-2θ XRD scans acquired from both $Ta_2C/Al_2O_3(0001)$ and $Ta_2C/hBN/Al_2O_3(0001)$ films with t = 17 nm exhibit only Ta_2C 0002n reflections (corresponding to c = 0.494 nm) while thicker layers (t = 75 nm) reveal the presence of additional 10 1 reflections. However, the 0002 reflection peak intensities are 5.4-fold stronger for the Ta_2C layers on $hBN/Al_2O_3(0001)$ than bare $Al_2O_3(0001)$. High-resolution TEM images and associated Fourier transforms indicate that the layers are single-crystalline. XRD ϕ scans show six 60°-rotated 1 0 -1 2 peaks of Ta_2C at the same φ angles for 1 1 -2 6 of Al_2O_3 based on which we determine the epitaxial crystallographic relationships between the film and the substrate as $Ta_2C(0002)$ || $Al_2O_3(0006)$ with in-plane orientation of Ta_2C[1 0 -1 0] || Al_2O_3[1 1 -2 0]. We further show that 0002-oriented Ta_2C thicker films can be obtained by inserting hBN layers at regular intervals during the deposition of thicker Ta_2C films.

9:20am **SE+NS+TF-MoM4 Nitride High Entropy Alloy Thin Films Deposited by Magnetron Sputtering and Cathodic Arc on Polymer Substrates: Structure and Electro-Mechanical Properties***, **Ao Xia**,* Montanuniversität Leoben, Austria*; R. Dedoncker,* Ghent University, Belgium*; M.J. Cordill,* Erich Schmid Institute of Materials Science, Austria*; D.J.M.G. Depla,* Ghent University, Belgium*; R. Franz,* Montanuniversität Leoben, Austria

In recent years a new class of materials has emerged in the field of metallurgy: high entropy alloys (HEAs). These metallic alloys consist of 5 to 13 metallic elements in an approximately equimolar ratio. Studies conducted on HEA bulk materials revealed promising combinations of properties, such as strength, ductility, corrosion resistance, wear resistance, hardness, diffusion and thermal conductivity. While research on bulk high entropy alloys has seen quite a boost over the past years, investigations on thin films are still a relatively unexplored area.

The focus of this report lies on the synthesis of MoNbTaVW HEA thin films by two different physical vapor deposition techniques, magnetron sputtering and cathodic arc deposition. The films were synthesized in Ar/N_2 atmosphere with varying gas flows in order to study the influence of N addition on structure and properties of the HEA thin films. Analysis by X-ray diffraction revealed a phase change from body-centered cubic (bcc) in case of the metallic HEA films to face-centered cubic (fcc) for the nitrides. A slightly lower N_2 gas flow is necessary in the case of magnetron sputter deposition to trigger the phase change than in the case of cathodic arc deposition. However, in both cases an increase in hardness was observed. For example, in the case of the films deposited by cathodic arc, the hardness increased from 18 to 30 GPa with the change from bcc to fcc phase. To further characterize the mechanical and electrical properties, the films were deposited on polymer substrates. The adhesion energy as determined from the geometry of buckles formed on the surface due to compressive stresses was a few J/m^2. In-situ uniaxial tensile tests revealed a brittle behavior of all films with crack onset strains of up to 3 %. The formation of elongated through thickness cracks caused a rather abrupt increase of the resistivity upon the crack appearance.

9:40am **SE+NS+TF-MoM5 Isomeric Phase Composition and Mechanical Properties of NbN Nanocomposite Coatings Deposited by Modulated Pulsed Power Magnetron Sputtering***, **Y.G. Li,** H. Yuan, Z.T. Jiang, N. Pan, M.K. Lei,* Dalian University of Technology, China

Isomeric NbN nanocomposite coatings on stainless steel substrate with face-centered cubic phase δ-NbN and hexagonal phase δ′-NbN were deposited by modulated pulsed power magnetron sputtering under nitrogen flow rate f_{N2} from 15% to 30%. It was found that the nitrogen flow rate f_{N2} had a significant influence on the energy delivered in each macropulse, which led to a marked change in the phase composition and mechanical properties. The peak power decreases from 54 kW to 16 kW as f_{N2} increases from 15% to 30% with the energy delivered in each macropulse from 23.2 J to 9.8 J. When f_{N2} is at 15%, NbN coatings are mainly composed of δ′-NbN phase which usually exists at high f_{N2} or under high compressive residual stress showing (100) and (102) preferred orientation, while δ-NbN gradually appears with the preferred orientation from (111) to (200) as f_{N2} increases accompanied with the decrease of δ′-NbN phase composition. The hardness and modulus of isomeric NbN nanocomposite coatings go up to 36 GPa from 30 GPa and 460 GPa from 366 GPa as f_{N2} increases to 20% with residual compressive stress from 0.47 GPa to 1.93 GPa, then decrease to 29 GPa and 389 GPa with residual compressive stress of 1.01 GPa showing a nonlinear response with peak power. The NbN nanocomposite coatings with more δ′-NbN phase show higher hardness and better toughness due to the composition variation of δ′-NbN and δ-NbN phases. The phase composition from δ′-NbN to δ-NbN phase should attribute to the delivered energy difference by peak power, and the anomalous increase in hardness should be originated from strengthening of the nanocomposite structure.

10:00am **SE+NS+TF-MoM6 Ab initio Guided Development of Ternary Borides: A Case Study of Ti-B-N, Ti-Zr-B, Ti-W-B, Ta-W-B, and V-W-B Systems***, V. Moraes, R. Hahn, M. Bartosik, H. Riedl,* TU Wien, Austria*; H. Euchner,* Ulm University, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; **Paul Heinz Mayrhofer,*** TU Wien, Austria

Transition-metal borides are a special class of ultra-high temperature ceramics. Among these, refractory borides such as TiB_2, ZrB_2, VB_2, TaB_2, and WB_2 are attractive candidates for many applications – ranging from high temperature electrodes, cutting tools, and molten metal containment to microelectronic buffer layers – because of their thermomechanical and chemical properties, their high melting temperatures up to ~3500 ºC, and excellent high temperature strengths. However, these diborides have a comparably low fracture toughness of K_{IC} ~1 MPa√m (here, basically obtained by in-situ micromechanical cantilever bending tests).

How diboride materials can be designed – implementing quantum chemistry guided materials design concepts – to allow for a combination of high strength, ductility, and thermal stability, is the focus of this talk. We will use recent developments of diborides – where we applied alloying and architecture concepts (e.g., composition and/or phase modulated layers) – to explore such materials-science-based guidelines for improved properties. Especially the phase stability (with respect to chemistry and temperature) of diborides is an extremely interesting task. For example, only WB_2 (among all binary diborides, except for TcB_2) provides a G/B ratio below 0.5 (~0.34) and a positive Cauchy pressure C_{13}–C_{44} (~73 GPa), which are typical indications for dominating non-directional bonds and thus a more ductile behavior. But WB_2provides these properties only in its metastable α-structure (AlB_2-prototype) and not for its thermodynamically stable ω-structure (WB_2-prototype). With the help of ternary diborides, such as $(Ti,W)B_2$ or even $(Ta,W)B_2$, the α-structure can be stabilized (even up to ~1200 °C). Even more important is a selective sensitivity of the α- and the ω-structure for the formation of vacancies. Especially, when using physical vapor deposition (PVD) techniques at moderate temperatures (here ~400 °C) the content of vacancies (and point defects in general) is rather high. Such defects are less penalized in the α- than in the ω-structure, allowing for growing even single-phased α-WB_2 by PVD, exhibiting hardnesses H of ~40 GPa combined with high fracture toughness of K_{IC} ~3 MPa√m.

With the help of superlattices, nanocolumnar and nanocomposite structures, we show that also with architectural concepts, strength (H ~45 GPa) and ductility (K_{IC} ~3.5 MPa√m) can be improved simultaneously.

The individual concepts will allow designing materials to meet the ever-growing demand for further improved coatings, tailor made for specific applications.

10:40am **SE+NS+TF-MoM8 Toughness Enhancement in Hard Ceramic Films by Alloy Design***, **Hanna Kindlund,*** Department of Mechanical and Aerospace Engineering, University of California Los Angeles (UCLA) **INVITED**

Transition-metal nitrides are refractory ceramics with high hardness, excellent wear resistance, high temperature stability, and good chemical inertness. Therefore, they are attractive in many applications, especially, as protective coatings against scratches, erosion, corrosion, and wear.

Tremendous efforts have been dedicated in enhancing hardness of ceramic films. However, in addition to high hardness, most applications also require high ductility, to avoid brittle failure due to cracking when coatings are subjected to high thermo-mechanical stresses. However, transition-metal nitrides, as most ceramics, are usually brittle, exhibiting low ductility and hence poor toughness.

Enhancing toughness in ceramic films is a challenging task that requires a fundamental understanding of the mechanical behavior of materials, which depends on their microstructure, electronic structure, and bonding nature. Theoretical studies using *ab initio* calculations predicted that alloys of VN with WN or MoN exhibit enhanced toughness as a result of their high valence electron concentrations, leading to an orbital overlap which favors ductility during shearing.

Here, I present experimental results on the growth of $V_{1-x}W_xN_y$ and $V_{1-x}Mo_xN_y$ alloy thin films, their microstructure, mechanical properties and electronic structure, and relate these properties with their enhanced ductility, demonstrating that it is possible to develop hard-yet-ductile ceramic coatings.

Surface Science Division
Room 203C - Session SS+HC+MI-MoM

Dynamical Processes at Surfaces

Moderator: Gareth Parkinson, TU Wien

8:20am **SS+HC+MI-MoM1 Light Induced Single-Molecule Dynamics at Surfaces***, **Wilson Ho,*** University of California, Irvine **INVITED**

Inhomogeneity of different length scales is one of the fundamental characters of matter that has its origin in the spatial variations of the charge and mass distributions. While many changes in nature and in the laboratory can be observed with the naked eyes, ultimately the interactions that lead to these changes occur at the atomic scale. In addition, heterogeneity influences the time scale that transformations occur at different locations, and the average time may differ significantly from the local times. The desire to understand and control changes in the charge and mass distributions would require experimental tools that possess simultaneous spatial and temporal resolutions to reveal the heterogeneity. This joint Å-fs resolution can be achieved by the combination of a femtosecond laser with a low temperature scanning tunneling microscope (fs-STM) that probes chemical transformations of single molecules. These experiments demonstrate the fs-STM approach in probing the effects of heterogeneity in space and time on the chemical dynamics in single molecules.

9:00am **SS+HC+MI-MoM3 Probing the Effects of Surface Structure on the Dissociative Chemisorption of Methane***, **Eric High**[1], D.G. Tinney, A.L. Utz,* Tufts University

Vibrational state-resolved reactivity measurements reveal details of fundamental processes that impact reactivity in the field of heterogeneous catalysis. Insights into energy flow during reaction obtained from observations of non-statistical mode-specific and bond-selective enhancements observed for methane and it's isotopologues on transition metal surfaces are one example. By providing reactive gas-molecules with precisely defined energy in well-defined energetic coordinates, state-selective experiments have also proven to be valuable probes of how surface atom motion affects overall reactivity. In this work, we will present vibrational state-resolved data collected via IR laser excitation of the antisymmetric stretch of supersonically expanded CH_4 gas molecules incident on a Ni(997) surface. We will focus on measurements investigating both the low and high incident energy regimes on this lightly stepped single crystal at a wide range of surface temperatures (T_S = 120 K to 1000 K). We will explore the possibility of benchmarking site-specific reaction barriers for dissociative chemisorption with molecules near the energy threshold for reaction. For higher energy molecular beams incident on higher surface temperatures, we will report on how the presence of steps on the Ni(997)

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

surface modifies the kinetics of surface-bound C diffusion into the Ni subsurface and bulk and how this process impacts subsequent methane reactivity on this surface.

9:20am **SS+HC+MI-MoM4 Adsorption and Diffusion of NH_3 on Anatase-TiO_2 (101)*, Kræn Christoffer Adamsen,* *S. Koust, E.L. Kolsbjerg, B. Hammer, S. Wendt, J.V. Lauritsen,* Aarhus University, Denmark

Fundamental understanding of catalytic processes for NO_x removal (Selective Catalytic reaction, SCR) is vital for improving existing catalysts and developing new. In the SCR cycle, NO_x is known to react from gas-phase on adsorbed ammonia on VO_x/TiO_2 based catalysts , and adsorption of ammonia on such oxides is therefore of great importance for fundamental understanding of NO_x-removal and SCR catalysis. Here we present a fundamental study of the static and dynamic behaviour of ammonia on anatase-TiO_2 (101), the predominant facet on anatase-TiO_2 nanoparticles. High resolution Scanning Tunnelling Microscopy (STM) of static adsorbed ammonia molecules at room temperature, indicates a strong binding to the surface. Through synchrotron radiation XPS ammonia was found to adsorb molecularly. The strong binding of ammonia was further quantified by Temperature Programmed Desorption (TPD) which also shows a highly coverage dependent binding energy, indicating molecular repulsion. All experimental obtained results are in accordance with a proposed theoretically calculated DFT-model of ammonia absorption.

Next, single ammonia molecule diffusion measured utilizing the high-speed Aarhus STM, show diffusibility to all neighbouring sites. Molecular repulsion also show a clear effect on static structures, where nearest neighbouring site occupation is rarely observed. Statistical analysis of intermolecular coordination supplied repulsion energies, which agree with observed values in TPD spectra and theory. For diffusion, we conclude that molecular repulsion increases the diffusibility for higher coordinated ammonia molecules. However when two ammonia occupy two nearest neighbour sites, they have the possibility of diffusing through a rolling effect, where ammonia can move more easily in one direction, this phenomena has also been seen for water on other oxide surfaces. Our analysis thus shows a surprisingly complex diffusion behaviour of NH3 on anatase TiO_2(101), which however resembles water dimer diffusion of water dimers on Rutile-TiO_2 (110).

9:40am **SS+HC+MI-MoM5 Non-equilibrium Growth of Metastable Clusters as a Means of Controlling Supramolecular Structure.***, Ryan Brown,* Clarkson University*; A.S.A. Kandel,* University of Notre Dame

This poster will review the use of non-equilibrium growth conditions to produce supramolecular structures not easily accessible using traditional self-assembly approaches. Specifically, the formation of cyclic, hydrogen-bonded clusters at the vacuum-solid interface following the direct injection of a solution into a high vacuum chamber gives insight into the utility of employing non-equilibrium growth conditions for producing supramolecular structures with metastable configurations. When deposited in a rapidly evaporating droplet, hydrogen bonding small molecules can form clusters with 5-fold symmetry if the correct combination of hydrogen bonding groups are present. These features persist at room temperature, but evolve into more complex structures upon mild annealing. Initial studies of this phenomenon in ferrocenecarboxylic acid, 1,1'-ferrocenedicarboxylic acid, indole carboxylic acid, and isatin will be discussed. Finally, future systems and directions of study will be discussed.

10:00am **SS+HC+MI-MoM6 Ultrafast Dynamics of Reaction Pathways on Metal Surfaces***, Jerry LaRue,* Chapman University

Important chemical processes often occur on the femtosecond timescale, requiring the use of femtosecond excitation and probing techniques to study them. Optical femtosecond laser pulses are a convenient method of initiating catalytically important reactions on metal surfaces, such as CO hydrogenation and CO oxidation, on the femtosecond timescale. Using femtosecond x-ray pulses from free electron lasers (FEL), we have selectively probed the bond making and breaking processes of these reactions using O and C k-edge x-ray absorption and emission spectroscopies to obtain time-resolved electronic structure maps. These electronic structure maps reveal the time evolution of different surface species along the reaction pathway, providing new insights into the reaction dynamics on metal catalysis. This talk will highlight past and recent results in reaction dynamics on metal surfaces as investigated using femtosecond x-ray pulses and supported through density functional theory (DFT) calculations and *ab initio* molecular dynamics (AIMD) simulations. Specific systems include CO desorption CO oxidation, and CO hydrogenation on ruthenium.

10:40am **SS+HC+MI-MoM8 Designer Solids via Multi-Heteroepitaxy: Layer-by-Layer Deposition of Molecular Frameworks on Solid Substrates***, Christof Wöll,* Karlsruhe Institute of Technology, Germany **INVITED**

Realizing molecular "Designer Solids" by programmed assembly of building units taken form libraries is a very appealing objective. Recently metal-organic frameworks (MOFs) have attracted a huge interest in this context. Here, we will focus on MOF-based electrochemical [1,2], photoelectro-chemical [3] and photovoltaic devices [4,5]. Internal interfaces in MOF heterostructures are also of interest with regard to photon-upconversion [6] and can be used for the crosslinking of sandwiched, reactive monomers [7]. Since the fabrication of reliable and reproducible contacts to MOF-materials represent a major challenge, we have developed a layer-by-layer (lbl) deposition method to produce well-defined, highly oriented and monolithic MOF thin films on a number of different substrates. The resulting films are referred to as SURMOFs [8]. The fabrication of hetero-multilayers (see Fig. 1) is rather straightforward with this lbl method. In this talk, we will describe the principles of SURMOF fabrication as well as the results of systematic investigations of electrical [9] and photophysical properties exhibited by empty MOFs and after loading their pores with functional guests. Furthermore, we will discuss further applications realized by loading MOFs with nanoparticles or quantum dots.

References:

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[9] J. Liu, T. Wächter, A. Irmler, P.G. Weidler, H. Gliemann, F. Pauly, V. Mugnaini, M. Zharnikov, Ch. Wöll, ACS Applied Materials & Interfaces, 7, 9824, (2015)

11:20am **SS+HC+MI-MoM10 Isotope Enrichment via Non-Equilibrium Differential Condensation and Reflection using Supersonic Beam Gas-Surface Scattering***, Jacob Graham,* *A. McMillan, K. Nihill, S.J. Sibener,* University of Chicago

Isotopically enriched materials have a variety of uses including chemical labeling, energy, medicine, and quantum computing. To stimulate the further development of these applications, modern, efficient isotope enrichment methods are needed. Non-equilibrium supersonic beam gas-surface scattering and differential condensation is shown to be a new and broadly applicable route to isotope enrichment. This enrichment is demonstrated with ^{36}Ar and ^{40}Ar isotopes reflecting from low temperature condensates of argon, with differences arising in the condensation coefficient, which depend on the degree of collisional energy exchange for each isotope at the interface. The enrichment factors were found to be tunable as a function of incident beam kinetic energy. For example, ^{36}Ar was found to be *enriched* relative to ^{40}Ar in the scattered fraction by greater than a factor of two, for a seeded beam of argon in helium having incident velocity 1650 m/s. In a separate and complementary experiment under the same conditions, the amorphous argon condensate was found to be *depleted* in its ^{36}Ar content, confirming this effect. This observed isotope selectivity during deposition introduces a new method for isotopic enrichment and purification as well as *in-situ* isotopic materials engineering.

11:40am **SS+HC+MI-MoM11 Structural Reorganization of Sequentially Adsorbed Two-component Self-assembled Monolayers after Soft Ultraviolet Irradiation***, C. Gerber,* ***Rebecca Quardokus,*** University of Connecticut

Sequentially adsorbed anthracene dicarboxylic acid and octanethiol on Au(111) form ordered regions of octanethiol, gold vacancy islands, and areas of disorder near domain boundaries and vacancy islands. Vapor deposition of octanethiol after drop-cast deposition of anthracene dicarboxylic acid on Au(111) results in small (√3 x √3)R30° and c(4x2) octanethiol domains. Initial exposure to soft ultraviolet irradiation increases disorder with only a few small close-packed octanethiol domains remaining. Repeated exposure to soft ultraviolet irradiation shows some removal of octanethiol molecules and sequential imaging by scanning tunneling microscopy gives snapshots of the stepwise reordering of the domains that ultimately leads to a structurally reordered monolayer consisting of larger domains of low-coverage octanethiol in a *p* x √3 structure.

Thin Films Division

Room 102A - Session TF1-MoM

Precursors and Surface Reactions

Moderators: Cathleen Crudden, Queen's University, Canada, Markku Leskela, University of Helsinki, Finland

8:20am **TF1-MoM1 Monitoring the Transient Surface Species during TiO_2 Atomic Layer Deposition using Surface-Enhanced Raman Spectroscopy***,* ***Ryan Hackler***[1]*, G. Kang, G.C. Schatz, P.C. Stair, R.P. Van Duyne,* Northwestern University

It is important to understand the dynamic surface chemistry that takes place during various atomic layer depositions (ALD) if high quality thin films with well-defined physical characteristics are to be achieved. In this work, ALD of TiO_2 was performed in tandem with *in-situ* surface-enhanced Raman spectroscopy (SERS) to monitor changes in the transient surface species present and to determine whether changes in the surface chemistry dramatically affect growth rate and purity. To ensure nucleation of the titanium precursor took place close enough to the plasmonic substrate necessary for SERS, a self-assembled monolayer of 3-mercaptopropionic acid (MPA) was used as a capture agent, with titanium tetraisopropoxide (TTIP) as the titanium precursor. Comparisons between the Raman spectra of the neat precursor and the SER spectra of the first ALD cycle of TiO_2 reveal typical ligand exchange chemistry, with self-limiting behavior and intact isopropoxide ligands. Subsequent cycles of TiO_2 ALD, however, show drastically different chemistry. No common vibrational modes between the neat precursor and the surface species are found in subsequent cycles, suggesting a lack of isopropoxide ligands. Continuous exposure of either TTIP or isopropanol after the 1st ALD cycle also results in atypical product formation coupled with unlimited CVD-like growth. Comparisons with alternative precursors (aluminum isopropoxide and titanium *tert*-butoxide) and DFT calculations reveal the isolated TiO_2 sites from the 1st ALD cycle play a role in the dehydration of isopropoxide ligands from subsequent TTIP doses. The resulting propene then undergoes oxidation with the help of the underlying plasmonic silver substrate before polymerizing into indistinguishable carbon products that accumulate on the surface. The observed dehydration chemistry is expected to be the result of the initial TiO_2 sites and is thus believed to be inherent when using TTIP as a precursor for TiO_2 ALD. As a result, considerations must be made regarding the viability of a surface for TiO_2 ALD using TTIP that were previously overlooked, such as reactivity to propene.

8:40am **TF1-MoM2 Theoretical Study on the Effect of Precursor Ligand in Atomic Layer Deposition of Al_2O_3 on SiO_2***,* ***Tania Sandoval,*** Universidad Técnica Federico Santa María*; T-L. Liu,* Stanford University*; R. Tonner,* Philipps-Universität Marburg*; S.F. Bent,* Stanford University

Atomic layer deposition (ALD) relies on the adsorption of metalorganic and inorganic molecules to create thin and conformal films for semiconductor device fabrication. Aluminum precursors, particularly trimethylaluminum (TMA), have been used for decades to deposit thin dielectric films. The reaction mechanism for this process is well known and reported in literature. However, with continued advances in semiconductor nanofabrication and thin film deposition, the ability to select precursors that meet different processing requirements is important. For this purpose, it is necessary to fundamentally understand the effect that the precursor structure can have on nucleation and growth. Thus, in this work, the adsorption of a series of Al-X molecules (X= $–CH_3$, –Cl, $–C_2H_5$, and $–C_3H_8$) on SiO_2 were explored. In the series, TMA is used as a model system and benchmark for comparison.

Density functional theory (DFT) calculations suggest interesting trends regarding the adsorption of Al-X molecules on SiO_2. Results indicate that when the number of Cl ligands on Al is increased, the dative bond that forms between the precursor molecule and the SiO_2 surface becomes more exothermic with respect to TMA. This increase is a result of electronic contributions to the total energy, which can be attributed to inductive effects caused by the addition of the Cl ligand. Additionally, it is observed that increasing the number of carbon atoms in an alkyl ligand stabilizes the dative bond; however, these surface adducts are primarily stabilized by dispersion interactions, which could be related to the ligand size. After initial adsorption of Al-X, either the alkyl or chorine ligand exchange reaction can proceed. Our DFT results suggest that exchange of the alkyl ligand is more thermodynamically favorable than that of the Cl ligand, which correlates well with the higher dissociation energy observed for Al-Cl versus Al-C.

Preliminary X-ray photoelectron spectroscopy (XPS) results for ALD using dimethylaluminum chloride and aluminum trichloride as precursors show chlorine at the silicon surface, suggesting only a partial ligand exchange reaction. These experimental results agree with our theoretical findings which show Cl-ligand exchange to be less thermodynamically favorable than the precursor state (dative bond). These results provide interesting insights into both the fundamental aspects of the adsorption chemistry of organometallic compounds on semiconductor surfaces and the practical aspects of designing precursor molecules for ALD growth.

9:00am **TF1-MoM3 Relevance of Dimeric and Tetrameric Structures to the Surface Chemistry of Metal Amidinate Atomic Layer Deposition Precursors***,* ***Bo Chen,*** *Y. Yao, Q. Ma, F. Zaera,* University of California, Riverside*; Y. Duan, A.V. Teplyakov,* University of Delaware*; J. Coyle, S. Barry,* Carleton University

The search for appropriate metallorganic compounds with clean chemistry has long been one of the central issues in atomic layer deposition (ALD) development. Metal amidinates have been shown to be excellent candidates for such purpose owing to their relatively simple synthesis methodology, fair volatility and reactivity, and ease with which they can be modified at the ancillary peripheral moieties. Recent studies of these compounds have suggested that they tend to dimerize, and in some cases even form tetramers, in the solid state. This finding raises important questions regarding the structures of metal amidinates during their vaporization, dosing, and activated adsorption in ALD process. In our study, three families of copper amidinate precursors, copper(I)-*N*,*N'*-di-*sec*-butyl-acetamidinate, copper(I)-*N*-*sec*-butyl-2-iminopyrrolidinate, and copper(I)-*N*-*tert*-butyl-5,5-dimethyl-2-iminopyrrolidinate, have been investigated to test the role of steric effects in ligand substituents on their surface chemistry over nickel and silicon oxide surfaces. It has been found that, by following specific ligand design strategies such as strengthening inner C–N bonds and preventing *β*-hydride elimination, it is possible to improve on the thermal stability of these precursors, and consequently on the chemical quality of the deposited films. Liquid-injection field desorption ionization mass spectrometry data proved that the dimeric and tetrameric structures of the copper amidinates in the solid state are retained upon vaporization into the gas phase (the dimers for the first and third compounds, a tetramer for the second), and X-ray photoelectron spectroscopy data pointed to the retention of the dimeric structure on the surfaces. Density-functional theory calculations of the relative energies of formation of the monomers, dimers, and tetramers confirmed the experimental results. The retaining of dimeric and tetrameric structures of metal amidinates upon initial adsorption implies that the dissociation of the dimers into the monomers on solid surfaces, as required in ALD processes, is likely to occur at high temperatures, to induce Cu reduction and ligand decomposition.

9:20am **TF1-MoM4 Low Temperature Dielectric ALD with the use of Hydrogen Peroxide: Comparison of Growth and Film Characteristics for Anhydrous H_2O_2, H_2O_2/H_2O Mixtures and H_2O***,* ***Daniel Alvarez,*** *K. Andachi, J. Spiegelman,* RASIRC

Novel precursor chemistries are being sought for ALD of dielectrics, where a tremendous amount of effort has been put into development of new Organometallic and Organosilicon precursors. Our approach focuses on providing a novel oxidant that may improve the reactivity of precursors that react slowly or incompletely with water. Our approach entails the development of two hydrogen peroxide gas delivery systems:

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[1] **National Student Award Finalist**

1. An ampoule based formulation for anhydrous hydrogen peroxide, where H_2O_2 is delivered in the gas phase in the absence of water by use of a membrane delivery system.
2. A gas generator approach, where a high concentration H_2O_2/H_2O mixture is delivered by in situ concentration methods and the use of a membrane vaporizer.

Anhydrous Hydrogen Peroxide Gas

Initial ALD results for growth of ZrO_2 from anhydrous H_2O_2 and $CpZr(N(CH_3)_2)_3$ show high quality film growth at 260C. A linear growth curve is observed with minimal saturation delay. ZrO_2composition was characterized by XPS and XRR, with results very similar to films grown with ozone. In addition, films resulting from H_2O_2 ALD were placed into MIMCAP structures. These structures show high k values of 35, slightly improved over those grown with a 20% ozone concentration at 32.

High Concentration Hydrogen Peroxide Gas

A novel gas generator for delivery of H_2O_2/H_2Omixtures has been developed. This equipment utilizes a carrier gas and delivers up to 5% H_2O_2/21% H_2O gas by volume from 30wt% H_2O_2 liquid solution (H_2O/H_2O_2=4.2). This gas mixture enables lower-temperature growth processes vs water, where HfO_2 films may be grown at temperatures as low as 100C.

Our current focus is on low temperature growth of SiO_2 ALD. Reactions of tris(dimethylaminosilane) $(N(CH_3)_2)_3SiH$ were performed with H_2O_2. Film characterization for anhydrous H_2O_2, H_2O mixtures, and water will be compared for films growth at 300C. Wet etch rates and refractive index will also be reported. Applications for multiple pattern spacers and hardmasks will also be discussed.

9:40am **TF1-MoM5 Putting More Chemistry into CVD. Precursors, Superconformality, and Selectivity*, Gregory Girolami*,** *J.R. Abelson,* University of Illinois at Urbana-Champaign **INVITED**

This talk will cover recent work on the synthesis of new CVD precursors for transition metals that combine air stability with good shelf life and high volatility, and studies of the mechanism by which they thermolyze. We will also describe our efforts over the last few years to develop new kinds of CVD methods that are able to deposit films both conformally and superconformally, as well as selectively on some surfaces but not on others. Our approach has been to think like chemists and to use kinetic concepts such as inhibition, differential diffusion, and rate laws to invent new methods to control film thickness as a function of depth. A variety of specific examples of our new approaches will be illustrated.

10:40am **TF1-MoM8 Insight into the "Residual Methyls" during ALD of Al_2O_3 from TMA/H_2O using *in situ* RAIRS*, Brent Sperling*,** *B. Kalanyan, J.E. Maslar,* National Institute of Sandards and Technology (NIST)

Despite being arguably the most well-studied and widely-used precursor pairing used for atomic layer deposition, trimethylaluminum (TMA) and H_2O continue to provide surprises. One of the most recent is the discovery that "residual" surface methyl groups persist at low temperatures even after large doses of H_2O, as observed using broadband sum-frequency generation (BB-SFG).[1] Our measurements using *in situ* reflection-absorption infrared spectroscopy (RAIRS) in a laminar-flow reactor have found evidence supporting the BB-SFG findings under typical ALD conditions. Post-deposition XPS measurements indicate that, in agreement with numerous other studies, very low concentrations of carbon are present in the resulting films even at low temperatures when residual methyls are present. With RAIRS, we observe a significant (approximately 10 cm^{-1}) reduction in the frequency of the deformation mode at ~1210 cm^{-1} after H_2O dosing. Small additions of H_2O allow the dynamics to be captured; as the intensity decreases and peak position changes, the peak shape remains constant. Explanations for the behavior are discussed along with suggestions on how this observation might be used to elucidate some the finer details of TMA/H_2O surface chemistry.

[1] V. Vandalon and W.M.M. Kessels, *Appl. Phys. Lett.***108**, 011607 (2016).

11:00am **TF1-MoM9 Low Temperature Atomic Layer Deposition of Silicon Nitride using Hexachlorodisilane and Ultra-High Purity Hydrazine*, Aswin Kondusamy*,** *A.T. Lucero, S. Hwang, X. Meng, H.S. Kim,* University of Texas at Dallas*; D. Alvarez Jr., J. Spiegelman,* RASIRC*; J. Kim,* University of Texas at Dallas

Silicon nitride is an important material in the semiconductor industry for applications in 3D integration and self-aligned patterning. The conventional processes used to deposit silicon nitride involve either high temperature or plasma to generate reactive species. Though they can produce good quality films in terms of electrical properties, wet etch rate and uniformity [1], they do not satisfy the demands for modern applications namely low thermal budget (<400 °C) and conformality over high aspect ratio structures. Newly developed ultra-high purity hydrazine sources have been successfully used to deposit metal nitrides at low temperature.[2] In this work, we studied the growth and properties of silicon nitride films deposited by low temperature Atomic Layer deposition (ALD) using Hexachlododisilane (HCDS) and Hydrazine.

Silicon nitride films were deposited in the temperature range 250-400 °C. The growth per cycle (GPC) gradually increased with hydrazine exposure and saturation behavior was observed. GPC of 0.4-0.5 Å/cycle is observed at 400 °C with refractive index of 1.813. X-Ray Spectroscopy showed that films of low oxygen (<2%) and chlorine (<1%) impurity can be achieved. These results are similar to those for films deposited with HCDS and NH_3 using Plasma-enhanced ALD at 360°C. Film density and wet etch rate results are compared for films deposited at different temperatures.

1. X. Meng, Y.-C. Byun, H. Kim, J. Lee, A. T. Lucero, L. Cheng, J. Kim, *Materials* 9 (12) 1007 (2016)

2. D. Alvarez, J. Spiegelman, R. Holmes, K. Andachi, M. Raynor, H. Shimizu, *ECS Transactions*, 77 (5) 219-225 (2017)

11:20am **TF1-MoM10 Investigating Low-Temperature Atomic Layer Deposition of Nickel Oxide using $Ni(^{tBu2}DAD)_2$ and Ozone*, Konner Holden,*** *J.F. Conley, Jr.,* Oregon State University*; C.L. Dezelah,* EMD Performance Materials

Nickel oxide (NiO), a wide band gap p-type oxide semiconductor, is of interest for applications in solar energy conversion [1], electrocatalysis [2], and as a tunnel barrier for metal/insulator/metal (MIM) diodes for infrared energy harvesting. Atomic layer deposition (ALD) is an ideal technique for the highly conformal, uniform thin films needed for these applications. Herein, we develop a new process for ALD of NiO using $Ni(^{tBu2}DAD)_2$ and O_3-.

ALD growth of metallic Ni has been demonstrated recently using $Ni(^{tBu2}DAD)_2$ and *tert*-butylamine [3]. ALD of metallic cobalt [4] and cobalt oxide [5] have been reported using $Co(^{tBu2}DAD)_2$ with formic acid and O_3, respectively. Here, we report the use of $Ni(^{tBu2}DAD)_2$ and O_3 for ALD of NiO. NiO was deposited in a Picosun Sunale R-150 using N_2-purge-separated cycles of $Ni(^{tBu2}DAD)_2$ held at 140°C and an O_3/O_2 mixture of ~10%. NiO films were characterized using variable angle spectroscopic ellipsometry (VASE) and grazing-incidence x-ray diffraction (GIXRD).

A plot of thickness vs. temperature for depositions using 135 cycles of a 5/30/4/30 s $Ni(^{tBu2}DAD)_2/N_2/O_3/N_2$ pulse sequence shows slightly decreasing growth with increasing temperature in the range of 175°C to 225°C (Fig. 1). In this temperature range, the refractive index is roughly constant at 2.38, consistent with reports for bulk and thin film NiO. Below 175°C, growth increases more steeply, likely due to condensation. Above 225°C, growth continues to decrease, due to desorption or possibly upstream precursor decomposition. A more detailed investigation of growth per cycle (GPC) versus temperature is underway. At 200°C, a linear GPC is observed, and saturating growth is observed for O_3 pulses of 4 s and longer, using a 5/30/x/30 s sequence (Fig. 2), while softer saturation is observed for $Ni(^{tBu2}DAD)_2$ pulses of 1 s and longer using a x/30/4/30 s sequence and is under further investigation. A GIXRD scan of an ~18 nm thick film deposited at 200°C indicates polycrystalline cubic NiO (Fig. 3).

Atomic force microscopy (AFM), x-ray reflectivity (XRR) and x-ray photoelectron spectroscopy (XPS) characterizing surface morphology, density, and composition, respectively, will be discussed at the meeting as well as dielectric properties (leakage, breakdown strength, dielectric constant, etc.) revealed by metal/insulator/metal (MIM) test devices.

[1] S. Seo et al., Nanoscale 8, 11403 (2016).

[2] K. L. Nardi et al., Adv. Energy Mater. 5 (2015).

[3] M. M. Kerrigan et al., ACS Appl. Mat. & Interfaces. 10, 14200 (2018).

[4] J. P. Klesko, M. M. Kerrigan, and C. H. Winter, Chem. Mater. 28, 700 (2016).

[5] J. Kim et al., Chem. Mater. 29, 5796 (2017).

Thin Films Division

Room 104B - Session TF2-MoM

IoT Session: Thin Film Processes for Energy Storage

Moderators: Virginia Wheeler, U.S. Naval Research Laboratory, Paul Poodt, Holst Centre / TNO, The Netherlands

9:00am **TF2-MoM3 Radical Enhanced Atomic Layer Deposition of Cobalt Oxide Based Electrodes for 3D Lithium-ion Battery Applications*, Ryan Sheil*,** *J. Lau, B. Dunn, J.P. Chang,* University of California at Los Angeles

Lithium-ion batteries have been an enabling factor in the success of consumer electronics and have the potential to offer energy storage solutions for microelectromechanical systems (MEMS). Current thin film battery technology consists of a two-dimensional planar stack of materials characterized by poor volumetric utilization where large areal footprints are required to supply the needed energy and power for device operation. Moving away from these traditional two-dimensional batteries towards next generation three-dimensional battery architectures (e.g. cylindrical arrays, interdigitated plates, etc.) allows for an effective decoupling of the areal energy and power density resulting in improved areal footprint utilization. In 3D architectures, the short distances between the anode and cathode improve the transport properties allowing for high areal power densities and the high aspect-ratio nature of the electrodes promotes high areal energy densities. Integration with these 3D architectures presents a challenge—requiring the synthesis of conformal thin films of both the electrolyte and counter-electrode, where optimization of the solid electrode/electrolyte interface is crucial for optimal device performance. Cobalt oxide is a potential candidate as a high capacity thin film anode material demonstrating lithiation capacities of 716 and 891 mAh/g for CoO and Co_3O_4, respectively.

The atomic layer deposition of cobalt oxide thin films was explored via a radical enhanced process employing the use of the metalorganic precursor, cobalt(II) (tmhd=2,2,6,6-tetramethylheptane-3,5 dione) and atomic oxygen, in addition to a thermal process involving H_2O. The growth rate of the radical enhanced CoO_x films was determined to be 0.3Å/cycle demonstrating a stable ALD temperature window from 190-230°C. The as-deposited cobalt oxide thin films demonstrated polycrystalline character on Pt(111)-Si substrates and a post deposition annealing treatment was utilized to further promote crystallization of the Co_3O_4 phase. A 75 nm CoO_x thin film demonstrated lithiation capacities ranging from 3,200 to 2,500 mAh/cm^3 at C/6 to 2C rates with a voltage cut-off of 0.4V vs. Li/Li^+. The discharge capacity and rate-ability were explored as a function of film thickness and post deposition annealing treatment conditions. Crucial in the realization of the all solid state 3D lithium-ion batteries is the optimization of the solid electrode/electrolyte interface. A solid electrolyte material, $Li_xAl_ySi_zO$, synthesized via a thermal ALD process utilizing H_2O as the oxidant source was integrated with the cobalt oxide electrode materials and their electrochemical properties explored.

9:20am **TF2-MoM4 Fast-charging 3D Battery Electrodes with High-Capacity Materials Using Large Area Atmospheric Pressure Spatial ALD*, Lucas Haverkate*,** *S. Unnikrishnan, D. Hermes,* Holst Centre / TNO, The Netherlands*; F. Roozeboom,* Eindhoven University of Technology, The Netherlands*; F. Zorro, F. Grob, E. Balder,* Holst Centre / TNO, The Netherlands*; P. Poodt,* Holst Centre / TNO and SALDtech B.V., Netherlands*; M. Tulodziecki,* Holst Centre / TNO, The Netherlands

The key challenges in next-generation all-solid state Li-ion battery technology development are related to the required energy and power densities, fast charging constraints, battery lifetime & safety hazards, and at the same time keeping the cost low by high-volume production. Such technology criteria require superior electrode as well as electrolyte materials (pinhole-free), and processing techniques enabling even advanced 3D designs. Apart from enabling fast-chargeability, 3D electrode architectures pave the way for the use of high-capacity materials without long-term cycling challenges.

However, newer architectures demand newer processing techniques, especially for conformal coating over three-dimensional structures. An technology researched fundamentally a lot in this respect is the Atomic Layer Deposition (ALD), which is well-known for its superior material quality and layer conformality over ultrahigh aspect ratio topology. But, in applications outside the advanced micro- and nanoelectronics industry, ALD technology is impeded by the economics of the low film deposition rates. Here, the scalable atmospheric pressure Spatial ALD (sALD) holds the best promise for sufficient deposition rates and large-area roll-to-roll processability, which is key to battery industry.

We will present about high-rate 3D Li-ion battery electrodes with sALD, which show charging speeds of 12 mins or less. Highlighted will be the development of new high performance battery electrode materials (in-situ doped titanate based) by engineering material properties at the nanoscale. Next to it, we will present about the *first-ever* sALD based LIPON electrolyte material (<100nm thick) exhibiting Li-ion conductivity > 10^{-7} S/cm. Such electrolytes are also relevant for development of protection layers in wet electrolyte-based Lithium ion batteries, as well as for enabling thin-film planar & 3D solid state batteries with ultrathin electrolyte layers (few 10s of nanometers thick). Other improvements aimed at stabilizing the solid-electrolyte interphase especially in wet Li-ion cells, maximizing ease of manufacturing and battery lifetime, will be part of the discussion as well.

9:40am **TF2-MoM5 Thin Film Technology - Opening New Frontiers for Solid State Batteries*, Gary Rubloff*,** *K. Gregorczyk,* University of Maryland, College Park*; A. Pearse,* Control Electron*; S.B. Lee,* University of Maryland, College Park*; A.A. Talin,* Sandia National Laboratories, Livermore **INVITED**

Solid state batteries (SSBs) offer several major advantages over the lithium ion rechargeable batteries that dominate today - most notably safety, design versatility that broadens the application space, and potentially higher performance. The safety benefit is largely ensured by avoiding flammable organic liquid electrolytes. Design flexibility is derived from the thin film processing approaches naturally employed in solid state batteries, accommodating various form factors consistent with patterning approaches at the heart of microelectronics manufacturing. A major step toward enhanced performance has recent emerged in 3D SSBs that deliver high power and energy, enabled by structures which extend to high aspect ratios. The promise they show is exemplified in SSBs based on thin film sputter deposition and more recently on atomic layer deposition (ALD), achieving a fully conformal 3D SSB with ALD multilayers serving as electrodes, solid electrolyte, and current collecting layers over high aspect ratio features. The resulting interdigitated 3D architecture exhibit the profound performance improvements expected. We consider the potential of this and other promising architectures, along with their pros and cons with respect to process sequence complexity and manufacturability.

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U.S. Department of Energy, Office of Science, Office of Basic

Energy Sciences (Award no. DESC0001160).

10:40am **TF2-MoM8 Atomic Layer Deposition: A Scalable Process for Enabling the Next Generation of High Performance Materials*, Arrelaine Dameron*,** Forge Nano **INVITED**

Atomic Layer Deposition (ALD) is a platform technology that has been widely demonstrated throughout the semiconductor industry, but is not yet widely accepted for modification of high surface area materials. However, R&D literature has shown ALD to impart significant processing and performance gains in all areas of advanced materials. For energy applications like energy storage and fuel cells, it has been perceived as slow and too expensive to consider as a realistic process for commercial adoption. However, Forge Nano has patented, constructed, and demonstrated a high throughput ALD capability at manufacturing scales, unlocking new potential for lower cost integration of ALD into products.

For example, in energy storage, as the mobility and portability requirements grow, so does the need for higher energy density materials, higher power density systems, and enhanced lifecycles of devices, all of which create additional stresses at interfaces within energy storage modules such as lithium-ion batteries, fuel cells, and supercapacitors. It is now widely accepted that the interfaces of lithium-ion battery electrode materials can be highly dynamic in nature, and are the source of detrimental effects such as electrolyte decomposition, particle fracturing, crystal phase transformations and other causes of performance fade. The next generation of energy storage devices will be designed and engineered with tailored interfaces to overcome some of these materials challenges. ALD is a critical tool for anyone attempting to modify interfaces at the R&D scale. Therefore, ALD should also be at the manufacturing scale to maintain an edge in a competitive market. This talk will discuss ALD as a means of controlling surface phenomena and its application for powder modification for a spectrum of technologies ranging from batteries to catalysis.

11:20am **TF2-MoM10 A Facile CVD Route for the Large-scale Fabrication of Silicon-graphite Core-shell Composites*, Giorgio Nava*,** *J. Schwan, L. Mangolini,* University of California, Riverside

Over the last decade, the research community engaged in significant efforts to investigate novel anode materials for Li-ion batteries with the goal of increasing the storage capacity of these devices. Among several candidates, silicon-carbon nanocomposites represent one of the most promising choices, featuring the highest theoretical gravimetric storage capacity. The small size of the silicon -Si- structures tackles the volume expansion undergone by the semiconductor upon lithiation, which causes pulverization of bulk Si electrodes, and promotes a robust cycling. The carbonaceous coatings, on the other hand, improve the electrical conductivity of the composite and prevent the direct interaction of Si with the electrolyte which in turn enhances the stability of the solid electrolyte interphase. Although a wide range of different Si-C nanocomposites have been investigated, these structures are often produced with methods characterized by questionable scalability, hence hindering the immediate introduction of these materials into actual manufacturing. In this contribution, we describe a facile and scalable-by-design approach for the fabrication of Si-core graphite-shell nanoparticles -NPs. Commercial Si NPs with an average size of 100 nm are introduced into a hot-wall furnace with an alumina combustion boat. The NPs are wrapped with a conformal coating of amorphous carbon resulting from the dissociation of acetylene - C_2H_2 - at 650 °C. After removing C_2H_2 from the reaction zone, the furnace is ramped up to 1000°C in Argon -Ar- yielding a controlled graphitization of the C-shell, as highlighted by Raman and TEM analysis, with no detectable presence of silicon-carbide. The as-produced composites are introduced into a slurry with no addition of conductive additives, coated onto a copper substrate and studied as pure anode material in Li-ion battery half-cell assemblies. The amorphous-C-coated Si NPs exhibit a high first cycle coulombic efficiency – CE – in the order of 87% and a capacity of 1800 mAh g^{-1} which rapidly decays below 1000 mAh g^{-1} during the first 40 cycles. The graphitization of the C-shell, achieved through the high-temperature step in Ar, significantly improves the cycling stability of the material showing a capacity above 1500 mAh g^{-1} over more than 100 cycles. Finally, the silicon-graphite composite is tested as a simple drop-in additive in graphite anodes. The addition of small amount of the Si-based active material (10% in wt) enables the fabrication of electrodes with a gravimetric capacity 30% higher than the one of the pure graphite electrodes used in commercial batteries, a first cycle CE of 90% and stable cycling over 100 cycles.

Tribology Focus Topic
Room 201A - Session TR+AS+NS+SS-MoM

Tribology Focus Session

Moderators: Mehmet Z. Baykara, University of California, Merced, Prathima Nalam, University at Buffalo - SUNY

8:20am **TR+AS+NS+SS-MoM1 Structural Superlubricity: History, Breakthroughs, and Challenges*, Mehmet Z. Baykara,*** University of California, Merced **INVITED**

The idea of *structural superlubricity* holds immense potential for the realization of nearly frictionless sliding in mechanical systems, with implications for fields as diverse as environmental conservation and space travel. The basic principle of structural superlubricity involves the proposition that friction should diminish at an interface formed by atomically-flat and molecularly-clean crystalline surfaces with different lattice parameters and/or incommensurate orientation. Despite the rather straightforward character of its basic principle, the realization of structural superlubricity under ambient conditions has been challenging due to the requirement of molecular cleanliness at the interface.

In this talk, we will first briefly review three decades of structural superlubricity research by emphasizing important milestones and breakthroughs. Subsequently, we will present results of nano-manipulation experiments from our lab, which demonstrate the remarkable occurrence of structural superlubricity for gold and platinum nano-islands sliding on graphite under ambient conditions. Complementary to the experiments, results of *ab initio* calculations will be discussed, which (i) reveal that the noble metal–graphite interface is expected to remain largely free from contaminant molecules, leading to structurally superlubric sliding under ambient conditions, and (ii) confirm the experimental observation of larger friction forces for platinum, attributable to higher energy barriers encountered during sliding. The experiments additionally demonstrate that the scaling power between friction force and contact size is independent of the chemical identity of the sliding atoms, but is determined by the geometric qualities of the interface. The talk will conclude with a review of remaining challenges for structural superlubricity, in particular those involving size- and deformation-related limits.

9:00am **TR+AS+NS+SS-MoM3 An Examination of the Nature of Bonding during Indentation and Sliding using MD and in-situ Nanoindentation*, Judith Harrison,*** United States Naval Academy **INVITED**

Adhesion between DLC tips and diamond counterfaces was examined using a nanoindentor coupled to TEM and molecular dynamics (MD). Additional MD simulations of sliding contact between the same tip-substrate materials were also carried out. Strong interactions between the surfaces in vacuum led to gradual nanoscale wear of the DLC. Force-separation curves show an approximate correlation between pull-off force and applied load for various contact points, while pull-in force was fairly constant for all contact points and independent of applied load. MD simulations were designed to replicate experiment as closely as possible and used the AIREBO and the REBO+S potentials. DLC tips with the same general shape (which often deviated from the assumed paraboloidal tip geometry due to wear) were brought into contact with diamond surfaces. MD results demonstrate that pull-off force is correlated with bonds formed during contact, providing an explanation of the trends observed in the TEM data. The effects of contact point and hydrogen-termination on pull-off forces and the nature of bond formation during sliding as a function of speed and hydrogen termination will be presented. The results of similar experiments and MD simulations using Si tips in contact with diamond counterfaces of adhesion and sliding using the ReaxFF potential will also be discussed.

9:40am **TR+AS+NS+SS-MoM5 The Chemistry of Friction, Wear, and Tribofilm Growth on 2D Materials*, Jonathan Felts,*** Texas A&M University **INVITED**

The evolution of a sliding interface between two objects is difficult to theorize, predict, and measure due to the complexity of the interface, which is often described phenomenologically. Here we utilized a nanometer sized single asperity of an atomic force microscope tip sliding against atomically flat graphene and graphene oxide to study the origins of friction, wear, and tribofilm growth phenomena at the atomic scale. We hypothesize that all of the observed contact phenomena at the macroscale can be described using fundamental thermochemistry. At low applied tip loads, the friction of graphene oxide is non-monotonic with tip velocity, initially increasing for speeds from 100 – 10,000 nm/s, followed by a decrease and a subsequent increase above 50,000 nm/s. At sufficiently high applied loads, we observe wear of oxygen groups from graphene oxide at temperatures between 50-400 °C and loads between 10-700 nN, and find an exponential increase in wear rate with applied load. For the case of an electrically biased tip oxidizing pristine graphene, the oxidation rate somewhat paradoxically increases with applied load, despite previously observed enhancement in wear rate with load. All of the above observations can be understood in the context of mechanically driven thermochemical reactions. The friction behavior depends on two competing factors—aging of the sliding contact due to chemical bonding between tip and substrate, and hopping of unbonded tip atoms between graphene lattice sites. Atomic wear of graphene oxide is well described by the tilted potential energy surface theory of mechanically driven chemistry, which predicts a non-linear reduction in the energy barrier with applied load. We further show that the tilted potential energy surface model also well describes the enhancement of oxidation rate. The work presented here creates a foundation for describing the mechanics of sliding contacts as chemical processes, and further paves the way towards quantitatively understanding how mechanical force drives chemical reactions in general.

10:40am **TR+AS+NS+SS-MoM8 Nanomechanics of Soft, Hierarchical Polymer- and Biological-Networks*, Prathima Nalam,*** University at Buffalo - SUNY **INVITED**

Soft networks based on synthetic polymer chains or biological filaments, with architecture that are anisotropic or hierarchical in nature, offer a path towards the development of tough and reliable flexible structures. These structures find applications in numerous areas including healthcare delivery, environmental purification systems, energy storage systems, flexible electronics, and tribology. Further, the ability of these networks to present a wide range of tunable functional properties, through alterations in the chemical structure of the monomers, synthesis or operational conditions, etc., which otherwise is rarely possible with other hard materials, promise the development of smart materials. In this study, we present the nanomechanical and nanotribological behavior of two stimuli-responsive networks consisting of (a) polyelectrolyte films with a thin layer of chitosan (CH) grafted on top of poly (acrylic acid) (PAA) brushes (CH/PAA) and (b) naturally grown mycelium-based networks. The CH/PAA network is a synthetic hierarchical structure, in which each layer exhibits a strong structural change with variation in solution pH. On the other hand, Mycelium is a soft biological network (derived from mushrooms) composed of multicellular or unicellular filaments, known as hyphae, with anisotropic micro-architecture.

A detailed investigation of the depth-dependent elastic moduli on these networks is conducted using atomic force microscope (AFM, Oxford Instruments) to study the impact of local structural heterogeneity of the network on its mechanical properties. A colloid-attached AFM cantilever was employed to study the surface interactions and to indent the material in the linear elastic deformation regime. The study of the impact of the network structure on the material rigidity, measured at both nano- and macro- scales, has enabled to probe the validity of affine network deformation theories for hierarchical networks. With this understanding, the design and development of antibacterial platforms (with CH/PAA platforms) and water-filtration membranes (with mycelium networks) using hierarchical soft structures is discussed.

11:20am **TR+AS+NS+SS-MoM10 Mechanisms for Controlling Friction and New Approaches for Achieving Superlubricity Regime in 2D Materials***, **Diana Berman**,* University of North Texas*; A. Erdemir, A.V. Sumant,* Argonne National Laboratory **INVITED**

Friction is an important aspect of many areas of everyday life. Varieties in mechanical systems from nano to macroscale and efforts to minimize energy losses intersect with challenges of controlling the friction. The popularity of recently discovered 2D materials and their usefulness for multiple applications enabled understanding the friction at a more fundamental level and opened new routes for manipulating friction to superlubricity or near zero friction values.

Here, we review the basic mechanisms that complies the frictional energy dissipation, such as wear, molecular deformation, thermal effect, electronic effect, bonding, environment and chemistry, phonons, and structural effect. We present the case studies highlighting how these mechanisms are controlled in 2D materials. Finally, we highlight recent advances in implementing 2D materials for friction reduction to superlubricity across scales from nano- up to macroscale contacts. We show that nanoscale superlubricity mechanisms originating from the formation of frictionless nanoscale systems, as in case of graphene-nanodiamond scrolls and carbon nanoonion structures, can be successfully transferred to macroscale effects. Development of 2D materials opened a new pathway for manipulating friction, which makes superlubric friction today's reality.

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Vacuum Technology Division
Room 203B - Session VT-MoM

Vacuum Measurement

Moderators: Marcy Stutzman, Thomas Jefferson National Accelerator Facility, Alan Van Drie, TAE Technologies

8:20am **VT-MoM1 Pharmaceutical Freeze-Drying and Vacuum-Drying: Challenges and Opportunities***, **Evgenyi Shalaev**,* Allergan **INVITED**

Many drugs are unstable in aqueous solutions, and drying is commonly used to improve their storage stability and shelf life. Freeze-drying is the most common drying method for parenteral pharmaceutical dosage forms, including both small molecular weight drugs and biologicals. Alternative vacuum drying technologies have also been introduced, although predominantly for research and development purposes. The presentation focuses on freeze-drying, starting with a brief overview of lyophilized (freeze-dried) products and corresponding manufacturing processes. The importance of pressure control during all three stages of freeze-drying (i.e., freezing, primary drying/ice sublimation, secondary drying / desorption of non-frozen water) is emphasized.

9:00am **VT-MoM3 Fixed Length Optical Cavities for Primary Traceability to the Pascal***, **Jay Hendricks**, J.E. Ricker, K.O. Douglass,* National Institute of Standards and Technology*; G. Brucker, E. Fuchs, A. Ocepek, P. Sullivan, S. Venkatesan,* MKS Instruments, Inc., Pressure and Vacuum Measurement Group

Over the past 5 years, NIST has worked to develop a new pressure standard based on the fundamental properties of gas refractive index that will replace mercury manometers at national metrology institutes and has potential to be developed as a commercially manufactured product. The new pressure standard is based a first-principles quantum-chemistry calculations of gas refractive index and is a new route to realizing the pascal. NIST has now built and tested a fixed-length optical cavity (FLOC), which consists a pair of Fabry–Pérot cavities within a single block of ultralow-expansion glass. The change in optical path length between the two cavities (one at vacuum and one at the pressure to be measured) depends on the gas refractive index, density, and atomic or molecular properties. Helium's atomic properties were calculated from first principles, so the refractivity measurement leads to a determination of density, which provides a determination of pressure. While helium's refractive index has now been calculated by theory, the value of nitrogen refractive index remains too difficult for current computational theory to handle. Using the NIST mercury manometer along with helium's theoretical value of refractive index in a FLOC has resulted in a new experimental value for nitrogen refractive index to be determined. This enables the FLOC to be used with nitrogen as a pressure standard with direct primary traceability to NIST. Moving forward, the FLOC technology is so promising as a pressure standard, that NIST has joined with MKS under a Collaborative Research and Development Agreement (CRADA). The aim of this partnership is technology transfer to the market place, with the aim to develop a small, portable prototype need for real world metrology operations for industrial applications in gas pressure metrology. The current status of NIST-MKS CRADA will be briefly presented and discussed.

9:20am **VT-MoM4 Fundamental Quantum-based Vacuum Metrology at NIST***, **Julia Scherschligt**,* National Institute of Standards and Technology

NIST has developed and characterized a variety of vacuum standards over the last several decades. Much effort, particularly recently, has been placed into developing standards based on optical methods and fundamental quantum properties. In this talk, I will present an overview of these efforts, focusing on the more recent advances in vacuum metrology. These span a wide range of pressures and employ a variety of nascent methods. However, our most recent methods focus on developing absolute standard based on fundamental physical properties, particularly quantum properties. At the low vacuum, we probe the pressure-dependent index of refraction of a gas in a fixed-length optical cavity (FLOC). At the middle range from the viscous flow regime to the high vacuum, we relate the ring-down time of a membrane to pressure ("Brane" gauge). At the ultra and extreme high vacuum (UHV and XHV), we use the loss-rate of ultra-cold atoms from a magnetic trap to measure background particle energy density in the cold-atom vacuum standard (CAVS). Each of these techniques presents unique technical challenges, I will put these challenges in context and briefly describe the research ongoing to address them. These include techniques to measure the refractivity of gases and distortion characterization for the FLOC, optomechanics and nanophotonics for the Brane gauge, and collision cross section measurements for the CAVS.

9:40am **VT-MoM5 Moving the FLOC to the Telecom***, **Kevin Douglass**, J.E. Ricker,* National Institute of Standards and Technology*; J. Hendricks,* National Institute of Standards and Technology (NIST)

Towards the goal of quantum based traceability of the SI, NIST has developed an optical pressure standard where traceability is achieved through accurate quantum mechanical calculations of the refractive index and virial coefficients of helium. To achieve widespread adoption of this novel optical pressure measurement technology we leverage the various technologies that have been developed to support the telecommunications industry. We have begun characterizing the performance of our Fixed Length Optical Cavity (FLOC) at 1542 nm. At this wavelength an acetylene stabilized laser can be used to measure the wavelength to better than a ppm, which is one of the requirements of the measurement. The new optical setup and methodology for achieving high accuracy will be discussed along with future challenges and a detailed look at the sources of uncertainty and methods for calculating pressure from the change in refractive index.

10:00am **VT-MoM6 Transient Method of Permeability Measurements for Microporous Media**, ***Martin-Victor Johansson,*** Aix Marseille University, France*; M. Wuest,* INFICON, Liechtenstein*; P. Perrier, I.A. Graur Martin,* Aix Marseille University, France

The gas flow through the low permeable porous media have a great interest, especially in vacuum technology for filtering, separation process, protection and flow control. It can combine high mass flow rate and a high level of rarefaction. This property makes it particularly suitable as a leak element, by taking advantage of the constancy of conductance in free molecular regime, for example for calibration of ionization gauges or mass spectrometer [1]. The transient experimental technique, developed previously for the mass flow rate measurements through the microchannels [2], is generalized to obtain the permeability directly from the pressure variation measurements. The present experimental methodology, allowing for step by step data verification, leads to higher accuracy than the similar and commonly used method such as "pulse-decay" techniques [3]. The measured data are fitted according to the exponential function with the pressure relaxation time as a single fitting parameter. The new expression for the permeability is proposed involving besides of the geometrical parameters, the ratio between the gas relaxation time (inverse of the gas collision frequency) and the pressure relaxation time. The permeability of the microporous media with the characteristic pore size of 0.2 and 0.5 microns is measured for different gases. It was found that the permeability at low pressure (3 Torrs) increases 50 times compared to atmospheric pressure permeability . This permeability increasing depends essentially on the gas nature.

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10:40am **VT-MoM8 Beamline Technology and Current Modeling Capabilities for Ion Implantation**, ***Svetlana Radovanov,*** Applied Materials, Varian Semiconductor Equipment **INVITED**

Ribbon beam technology have been used in semiconductor ion implantation for past three decades. Over the years these ion implanters have become highly sophisticated tools incorporating the use of energy filters, collimators, quadrupoles, scanning systems and more recently molecular plasma sources, cryogenic and elevated implant temperature capabilities. One of the features that made these tools so successful in device fabrication is the high degree of control of the dopant depth profile. By selecting a unique ion mass, ion charge, ion energy and implant angle, a beam line tool offers highly automated control over the beam transport and implanted ion dose [1]. These beam lines operate with a large variety of species, several orders of magnitude energy and dose range. The wafer processed per hour reach 500 wafers/hour for a standard high current implanter. In recent years, some very high dose applications have been enabled by plasma doping systems [2]. For example, some dynamic random-access memory applications require incredibly high doses ~$5x10^{16}$ /cm^2 that can be done by plasma doping systems. Unlike the beam line tools, ions are not mass analyzed, but instead the wafer is processed within the plasma chamber or in an adjacent vacuum chamber. The wafer is pulsed negatively by a bias supply with a square wave T~50ms and f~5-50 kHz. Implant energy is controlled by the bias voltage which can exceed 10 kV. The plasma is generated by an inductively coupled rf coil. When the bias voltage is on, a plasma sheath forms in front of the wafer surface, across which ions are accelerated and are implanted into the silicon.

In this paper, we will discuss electrostatic focusing, filtering and steering of an ion beam and modeling associated with it. This will include low energy beam acceleration, deceleration and transport. We also describe the 2D and 3D codes that are used to model beam line optical elements.

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11:20am **VT-MoM10 Design of a New Thermal Vacuum Chamber for Space instrument Calibration**, ***Freek Molkenboer,*** *R. Jansen, R.G. Veraar, G.C.J. Otter, W.P. van Werkhoven, N.B. Koster, F.P.G. Driessen,* TNO, Netherlands

TNO is investing in a new facility for calibration of optomechanical Space instruments. This facility, called Calibration Space Instruments (CSI) should be operational early 2021. To meet this deadline the conceptional design phase has started early 2018.

The facility has three major sub system; a Thermal Vacuum Chamber (TVC), an Optical Ground Support Equipment (OGSE) and a Mechanical Ground Support Equipment (MGSE).

The OGSE system will provide all the optical stimuli that are required to perform an optical calibration of a Space instrument.

During a calibration of a Space instrument many relative positions between the OGSE and the instrument must be tested. The MGSE is responsible for the high accuracy, and highly reproducible manipulation of both the OGSE and the instrument. It is expected that some of the manipulation is done in vacuum, leading to the corresponding challenges.

The calibration of the instrument must be performed at the temperature in which it will operate in orbit. The TVC needs to provide these conditions. Beside the operational temperature the instrument also needs to be tested at non-operational temperatures, which increases the temperature range. It can be expected that some parts of the instrument will require LN2 temperatures. The CSI facility will focus on calibration of mid-size instruments, this results in a chamber with a volume up to 15 cubic meter

The vacuum pressure during a calibration shall be below 10-5 mbar. The challenge is that the materials used in a Space instrument and the TVC absorb a lot of water when exposed to air, resulting in a high pumping speed needed to reach the required pressure.

Future Space instruments will have higher resolution, which will directly impact the calibration facility. To be able to perform a calibration, pointing accuracies of 0.0015° are needed, which might result in for instance active shielding of vibrations from the TVC system and the floor towards the instrument and the OGSE.

Space instruments represent a lot of money, therefore instrument safety is crucial in the design of the facility.

During the oral we will discuss challenges that come with the design of the TVC for Space instrument calibration, and the measures that are taken to ensure safe and successful calibration campaigns.

11:40am **VT-MoM11 Pressure Measurements from Combining Non-evaporable Getter Pumps and a Novel Extreme High Vacuum Cryopump**, ***Marcy Stutzman,*** Thomas Jefferson National Accelerator Facility*; A. Segovia Miranda,* Universidad Aut´onoma de Zacatecas*; P.A. Adderley, M. Poelker,* Thomas Jefferson National Accelerator Facility

The Jefferson Lab polarized electron source requires vacuum approaching extreme high vacuum for long operational lifetime for the GaAs photocathodes. Currently the system is pumped with a combination of non-evaporable getter (NEG) pumps, ion pumps, and a NEG coating on the chamber walls. Exploring further improvement of the vacuum for the system, we have assembled a system using an array of NEG modules and a novel cryopump with Boron Nitride Nanotubes (BNNT) instead of the traditional charcoal. The BNNT has been mechanically attached to the cryosorption surfaces of a commerical cryopump, and the system fully baked to remove water with no adhesive present in the system. We report here on the pump speed of the BNNT cryopump, and characterize the base pressure achieved in the combined NEG/cryopump system using both an extractor gauge and a Watanabe 3BG XHV ionization gauge which has reached at least the x-ray limit of the extractor gauge.

2D Materials Focus Topic
Room 201B - Session 2D+MI+NS-MoA
2D Materials Characterization including Microscopy and Spectroscopy

Moderators: Stephan Hofmann, University of Cambridge, UK, Richard Vanfleet, Brigham Young University

1:20pm **2D+MI+NS-MoA1 Observing the Mechanisms of Graphene Growth during Chemical Vapor Deposition: Routes to Controlling Layer Number and Domain Size***, **Robert Weatherup**,* University of Manchester, UK **INVITED**

Chemical vapor deposition (CVD) on polycrystalline metal foils has emerged as the most economic and versatile means for producing 2D materials over large areas,[1] and directly integrating them with other device materials to achieve new functionality.[2] To tailor these materials to specific applications, a detailed understanding of the underlying growth mechanisms is required such that parameters such as domain size, defect density, and layer number can be precisely controlled. However, the elevated temperatures and reactive gas environments involved in growth make direct observation challenging, whilst ex situ measurements are often ambiguous.

Here we apply environmental scanning electron microscopy (ESEM) and ambient pressure X-ray photoelectron spectroscopy (APXPS) to directly observe graphene growth under realistic CVD conditions on polycrystalline Pt foils.[3] This reveals a variety of processes involved in graphene formation including isothermal growth by direct hydrocarbon dissociation, isothermal dissolution into the catalyst bulk, and precipitation on cooling. The balance of these processes, and thus growth outcome, is shown to depends critically on the distribution of carbon close to the catalyst surface, which is in turn is intimately linked to the processing profile.We thereby develop a growth model for graphene CVD that considers precursor dissociation, mass-transport, attachment to the edge of growing graphene domains.[4] This is shown to generally applicable to several transition metal catalysts,[5] and serves as a general framework for understanding and optimizing the growth of 2D materials on polycrystalline catalysts.

We thus demonstrate that the CVD process can be rationally designed to yield different desired growth outcomes from the same polycrystalline starting catalyst, including uniform SLG with large domain sizes (>100 µm), large isolated BLG domains (>50 µm), and uniform BLG. Our result show that through targeted operando experiments the influence of key process parameters can be established, enabling precise control over 2D material growth including domain sizes and layer number.

1. S. Hofmann et al. *J. Phys. Chem. Lett.* **6,** 2714–2721 (2015).
2. M. Piquemal-Banciet al. *Appl. Phys. Lett.* **108,** 102404 (2016).
3. R. S. Weatherupet al. *Nano Lett.* **16,** 6196–6206 (2016).
4. R. S. Weatherupet al. *ACS Nano* **6,** 9996–10003 (2012).
5. A. Cabrero-Vilatela et al. *Nanoscale* **8,** 2149–2158 (2016).

2:00pm **2D+MI+NS-MoA3 Band Alignment of 2-D Materials by Internal Photoemission***, Q. Zhang, S. Zhang,* Theiss Research & National Institute of Standards and Technology*; B. Sperling,* ***Nhan Nguyen,*** National Institute of Standards and Technology

Two-dimensional (2-D) materials have brought new possibilities for the future electronic and optoelectronic applications [1], [2]. Electronic band alignment at the interface is one of the important parameters in many device designs. For instance, staggered band alignment is preferred to separate photon generated electron-hole pairs in optoelectronic and photovoltaic devices [3]. For the 2-D materials in the monolayer (ML) limit, it has been a challenge to accurately measure the electron affinity which determines how the bands align at the interface. In fact, most 2-D heterojunctions are designed using calculated or theoretically predicted band alignments [4]. In this work, we present an experimental measurement using internal photoemission spectroscopy (IPE) to determine the band offset of MX$_2$ semiconductors (M = Mo, W; X = S, Se) in relative to an oxide barrier and suggest possible combination of the MX$_2$ materials to be used for optoelectronic and photovoltaic applications. This IPE approach is seen as a unique method that can be applied to characterize other 2-D materials.

The IPE test structure is fabricated by exfoliating MX$_2$ flakes on to the Al$_2$O$_3$/p^+Si substrate and depositing Ti/Pt contacts on the flakes with large open areas for light absorption. By using gold film mediated exfoliation method [5], large area (> 75 x 75 µm^2) ML MX$_2$ flakes are obtained, confirmed by Raman spectrum and photoluminescence mapping. Photocurrents of the MX$_2$-Al$_2$O$_3$-p^+Si structure are measure with the incident photon energy swept from 2.0 eV to 5.5 eV and gate voltage V_{GS} (applied to the Si back gate) stepped from -1.0 V to 1.6 V. The oxide flat band voltage (V_{FB}) is extracted by the voltage where the photocurrent switches sign near and above photoemission thresholds. The band offsets at the MX$_2$/Al$_2$O$_3$ and Al$_2$O$_3$/Si interfaces are extracted as the thresholds of the cube root of photoemission quantum yield (Y) being the ratio of the photocurrent over the incident light flux [6]. At gate bias below V_{FB}, the band offset between Al$_2$O$_3$ and Si is measured and found to be 3.4 eV for all the 4 devices, which is also a well-established value. More importantly, the band offset at the MX$_2$/Al$_2$O$_3$ interfaces combined with the known optical band gaps of ML MX$_2$ suggest that MoS$_2$/WS$_2$ and MoSe$_2$/WSe$_2$ can possibly form the staggered heterojunction.

[1] G. Fiori, et al, Nat. Nanotech. **9**, 768 (2014).

[2] F. Xia, et al, Nat. Photonics **8**, 899 (2014).

[3] X. Hong, et al, Nature Nanotech. **9**, 682 (2014)

[4] J. Kang, et al, Appl. Phys. Lett. **102**, 012111 (2013)

[5] S. B. Desai, et al, Adv. Mater. **28**, 4053 (2016).

[6] V. V. Afanasev and A. Stesmans, J. Appl. Phys. **102**, 081301 (2007).

2:20pm **2D+MI+NS-MoA4 Visible to mid-IR Nanoscale Characterization of 2D Materials via Photo-induced Force Microscopy***, **Padraic O'Reilly**, D. Nowak, S. Park,* Molecular Vista

While several 2D materials have been studied with scattering scanning near-field optical microscopes (s-SNOM) with nanoscale spatial resolution, most have focused on the study of surface phonon polariton (SPP) [1]. In this paper, we introduce a relatively new technique called photo-induced force microscopy (PiFM), which combines atomic force microscope (AFM) and broadband optical spectroscopy to analyze both topography and polarizability of samples with sub-10 nm spatial resolution [2]. With PiFM, the near-field optical information is acquired by measuring the photo-induced force between the AFM tip and the sample rather than by collecting photons with a far-field photo-detector; this near-field excitation and near-field detection configuration provides excellent signal-to-noise without the far-field background signal from the much larger focal spot, making the technique robust and easy-to-use. With mid-IR sources, PiFM can image nanoscale SPP as with s-SNOM. With supercontinuum visible-infrared light source, it can directly probe the exciton resonances with equally impressive spatial resolution. With its capability to image number of layers, quality of samples, and plasmonic fields, PiFM is an ideal nanoscale characterization tool for wide range of 2D materials. Results from graphene, MoS$_2$, WS$_2$, and hBN will be presented.

[1] T. Low et al., Nature Materials 16, 182–194 (2017).

[2] R. A. Murdick et al., Jap. J. of Appl. Phy., 56, 08LA04 (2017).

2:40pm **2D+MI+NS-MoA5 Polymorphic Structures and Diversified Properties of Low-dimensional Materials Investigated by In situ Electron Microscopy***, **Kazu Suenaga**,* National Institute of Advanced Industrial Science and Technology (AIST), Japan **INVITED**

Two-dimensional transition metal dichalcogenides (TMDs), consisting of an atomic plane of a transition metal (M: Ti, Nb, Mo, Re, etc.) sandwiched between two chalcogen atomic planes (X: S, Se, Te). This crystalline structure combined with a wide variety of constituent elements give rise to diverse electronic properties, strongly governed by the number of its *d*-orbital electrons. MoS$_2$ and WS$_2$ are the most representative “group 6” TMDs featuring trigonal prismatic (H) phase semiconductor with a direct band gap. The TMDs can exhibit various polymorphs and present different electronic properties as the atomic arrangement changes originating from charge transfer. A metallic octahedral (T) phase has been reportedly stabilized by alkali metal intercalation [1], and another distorted octahedral phase zigzag-shape phase (Z) with clusterization of metal atoms into zigzag chains by using solvent-based exfoliation. Some simulations indicate that the Z phase may undergo the Peierls distortion and be transformed into a diamond-shape (DS) phase where atoms reconstruct in a way that four metal atom appear as a diamond (rhombus) in the plane [2]. We show in this talk the experimental evidences for these polymorphic structures and diversified properties found in a family of 2D TMDs.

These monolayer forms in TMDs are typically the same as a single layer of the bulk material. However, PdSe$_2$ presents a puzzle. Its monolayer form has been theoretically shown to be stable, but there have been no reports that monolayer PdSe$_2$ was fabricated. Here, we demonstrate that the preferred monolayer form of this material amounts to a melding of two bulk monolayers accompanied by the emission of Se atoms so that the resulting stoichiometry is Pd_2Se_3[3].

[1] Y.-C. Lin, D. O. Dumcenco, Y.-S. Huang and K. Suenaga, *Nature Nanotechnology*, 9 (2014) pp.391-396

[2] Y.-C. Lin, H.-P. Komsa, C.-H. Yeh, T. Bjorkman, Z.-Y. Liang, C.-H. Ho, Y.-S. Huang, P.-W. Chiu, A. V. Krasheninnikov, and K. Suenaga, *ACS Nano* 9 (2015) pp.11249-11257

[3] J. Lin, S. Zuluaga, P. Yu, Z. Liu, S. T. Pantelides, and K. Suenaga *Phys. Rev. Lett.*, 119 (2017) 016101

[4] This research was supported by JSPS KAKENHI (JP16H06333 and JP25107003).

3:40pm **2D+MI+NS-MoA8 Probing Interlayer Interaction in van der Waals Materials by Low-energy Electron Microscopy (LEEM)*, Johannes Jobst*,** *D. Geelen,* Leiden University, Netherlands*; R.M. Tromp,* IBM, T.J. Watson Research Center*; S.J. van der Molen,* Huygens-Kamerlingh Onnes Laboratory, Netherlands **INVITED**

Knowledge on the interaction between layers is crucial to tailor the properties of van der Waals (vdW) materials. We investigate these using newly developed techniques based on low-energy electron microscopy (LEEM). With LEEM, we probe the reflection of electrons as a function of incoming energy (0-100 eV). We have recently extended our UHV instrument to also measure low-energy electron transmission (eV-TEM).

We apply LEEM and eV-TEM to few-layer graphene. With each layer, an unoccupied interlayer state is added, which hybridizes with the other states. In LEEM, the resulting eigenstates appear as minima in the reflection spectrum. In transmission, they show up as maxima. From both functions, we determine the hybridization energies of the interlayer states, which extend in 2D.

Next, we study the 2D-dispersion relations of these states. For that, we have developed *angle-resolved reflected-electron spectroscopy* (ARRES) [1]. With ARRES, we investigate few-layer graphene, hBN, as well as their combination. For the latter case we find negligible interaction. [2]

[1] Jobst *et al.*, Nat. Comm. **6**, 8926 (2015)

[2] Jobst *et al.,* Nat. Comm. **7**, 13621 (2016)

4:20pm **2D+MI+NS-MoA10 Fast Full Wafer Analysis for Graphene and 2D-materials by Imaging Ellipsometry*, Sebastian Funke,*** Accurion GmbH, Germany*; P. Braueniger-Weimer, S. Hofmann,* University of Cambridge, UK*; P.H. Thiesen,* Accurion GmbH, Germany

By combining the resolution of optical microscopy and the sensitivity of thin films, imaging ellipsometry (IE) is a powerful tool to characterize thin materials. It allows to measure monolayers of 2D-materials but also to visualize these monolayers on arbitrary substrates. It overcomes the need of specially tuned SiO_2 thicknesses to visualize e.g. Graphene in an optical microscope.

In the talk we present [1], the characterization of Graphene throughout all stages of the manufacturing process from the growth on Cu-foil up to the transferred sample on Si wafers. Unlike other methods IE directly visualizes graphene on the rough Cu. We apply IE to resolve a large area map of Graphene on Cu. The Graphene is directly characterized on the Cu-foil, no oxidation of the Cu is needed. To overcome the waviness of the foil, an autofocus algorithm is developed and applied.

IE is also able to distinguish a Graphene monolayer and hBN monolayer after the transfer process to a Si/SiO_2 substrate. We show large area map of the transfered sample. The contrast mode of IE is able to distinguish the different regions: (a) substrate only, (b) hBN only, (c) Graphene only and (d) an overlapping region of hBN and Graphene. The complete sample approx. 1cm x 0.8 cm is recorded in less than 6 minutes and shows defects and wrapping of hBN of a size as small as 4 µm.

Lastly, we apply IE to characterise full 4’’ wafers of graphene on Si.

[1] Braueniger, Funke et al. submitted

Applied Surface Science Division
Room 204 - Session AS-MoA

Multitechnique Applications-When More techniques are Better than One

Moderator: Karen Gaskell, University of Maryland, College Park

1:20pm **AS-MoA1 Overcoming Obstacles in Surface and Interface Characterization of All Solid-State Lithium Battery Materials*, Natalie Seitzman,*** Colorado School of Mines*; H. Guthrey, D. Sulas, S. Johnston,* National Renewable Energy Laboratory*; J. Nelson Weker,* SLAC National Accelerator Laboratory*; H. Platt,* Solid Power, Inc.*; M. Al-Jassim,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines

Novel battery technologies are a key route to sustainable energy, but new chemistries come with new failure mechanisms that present characterization challenges. The nature of many promising next-generation batteries makes them inherently difficult to study, and multiple techniques must be combined to capture the relevant phenomena. For all-solid-state lithium batteries, one challenge is the reactivity of the battery components restrict which types of techniques may be used. Additionally, although the interfaces are of great interest, processes that expose them for characterization have unknown, likely deleterious effects on their integrity. Therefore, in order to understand characterization of surfaces and interfaces in batteries, bulk characterization and in situ characterization at multiple scales is also needed.

The focus of this work is probing the morphological evolution, including dendrite formation, of the electrode-electrolyte interface between lithium metal and β-Li_3PS_4 solid electrolyte. This is done through a combination of lock-in thermography, x-ray tomography, in situ scanning electron microscopy (SEM), and x-ray absorption near edge structure (XANES). We used thermography as a first step to identify trends in location of dendritic features, to guide techniques with smaller fields of view and greater resolution, such as SEM. X-ray tomography enables characterization of the interfaces without deconstructing the device or exposing the interfaces needed for surface characterization. Therefore, micro-tomography was performed both to study morphological changes and to check that results observed in other experiments with modified samples—such as nano-tomography, which required a focused ion beam to cut and lift out micron-scale samples—are consistent with the behavior of unaltered materials. In situ SEM cycling experiments and windowless energy dispersive spectroscopy (EDS) provided morphological and chemical characterization of the changing surfaces and interfaces with high spatial resolution. Detailed chemical characterization of the bulk material was obtained with XANES at the sulfur and phosphorus K-edges. This work furthers the development of surface and interface characterization of battery materials and moves toward localized, nanoscale characterization.

1:40pm **AS-MoA2 *In-situ* Complementary XPS and Raman Analysis of Technologically Important Materials*, Paul Mack,*** Thermo Fisher Scientific, UK

In this work, X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy have been used to analyse technologically relevant materials. An XPS spectrometer (Thermo Scientific Nexsa) was configured with a Raman spectrometer, enabling *in-situ* complementary analysis. XPS is a surface sensitive technique, with an information depth between 0-10nm. It is chemically selective, allowing the use to investigate different bonding states of the same element. Raman is a vibrational spectroscopy, which is more bulk sensitive (typically on the µm scale). It can also give some information about chemistry, but it also yields complementary structural or bonding information.

The battery-relevant material, lithium cobaltite ($LiCoO_2$) was analysed in the Nexsa spectrometer. $LiCoO_2$ is used in the cathode of some lithium-ion batteries. During charge/discharge cycling the cathode may degrade, causing the creation of the mixed oxide, Co_3O_4. XPS and Raman data were acquired from two different points on a $LiCoO_2$ cathode. Differences in cobalt and lithium bonding states at the surfaces of the two different points were analysed with XPS, before and after argon ion cleaning. Complementary Raman analyses were performed at the same points in the same instrument. The Raman data allowed identification of the bulk material, together with an evaluation of cobalt oxide degradation products.

The second sample analysed in this work was a boron nitride film deposited onto a copper substrate. The goal of the deposition was to create an atomically thin hexagonal boron nitride structure (h-BN), analogous to graphene. It was found that the deposition created an inhomogeneous distribution of boron nitride, which was optically invisible. XPS mapping and imaging (Thermo Scientific SnapMap) was used to locate the boron nitride on the copper substrate. The XPS image was used to define the analysis points for further XPS and Raman analysis. XPS allowed the chemical bonding states of the boron and nitrogen to be identified, together with an identification of contaminants on the surface. The structure of the boron nitride, such an sp^2 and sp^3 configurations, was evaluated with Raman spectroscopy.

2:00pm **AS-MoA3 Integration of Laboratory Experiments. Spectroscopy, and Microscopy to Investigate the Reactivity of Metals in Mine Wastes*,* *José Cerrato,*** University of New Mexico **INVITED**

The reaction mechanisms affecting metal transport in mine waste sites was investigated by integrating laboratory experiments, microscopy, and spectroscopy. Metal release from these mine wastes could pose potential health risks for neighboring communities. Spectroscopy analyses on the first site located in Northeastern AZ (Navajo tribe) suggest that U-V phases are present in abandoned mine wastes; the dissolution of these U-V phases is relevant to U and V transport. Electron microprobe and electron microscopy analyses on the second site located in Laguna, NM (Pueblo tribe) suggest that U-Si and U-P phases on mine wastes from which could be a source for U in neighboring surface waters. The presence of U(VI) and U(IV) was detected with X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). The presence of coffinite encapsulated in particulate organic matter was identified in mine waste samples using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Accumulation of U in roots of plants from these mine waste sites was also investigated.

3:00pm **AS-MoA6 Surface Phase, Morphology, and Charge Distribution Transitions on Vacuum and Ambient Annealed Perovskites: A Case Study on $SrTiO_3$(100)*,* *Omur Dagdeviren*[1]**, *G. Simon, K. Zou, C. Ahn, F.J. Walker, E.I. Altman, U.D. Schwarz,* Yale University

The surface structures of $SrTiO_3$(100) single crystals were examined as a function of annealing time and temperature in either oxygen atmosphere or ultrahigh vacuum (UHV) using noncontact atomic force microscopy (NC-AFM), Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED) [1]. Samples were subsequently analyzed for the effect the modulation of their charge distribution had on their surface potential. It was found that the evolution of the $SrTiO_3$surface roughness, stoichiometry, and reconstruction depends on the preparation scheme. LEED revealed phase transitions from a (1×1) termination to an intermediate $c(4\times2)$ reconstruction to ultimately a $(\sqrt{13} \times \sqrt{13})-R33.7°$ surface phase when the surface was annealed in an oxygen flux, while the reverse transition from $(\sqrt{13} \times \sqrt{13})-R33.7°$ to $c(4\times2)$ was observed when samples were annealed in UHV. When the surface reverted to $c(4\times2)$, AES data indicated decreases in both the surface Ti and O concentrations. These findings were corroborated by NC-AFM imaging, where initially TiO_2-terminated crystals developed half-unit cell high steps following UHV annealing, which is typically attributed to a mix of SrO and TiOSrO and TiO_2terminations. Surface roughness evolved nonmonotonically with UHV annealing temperature, which is explained by electrostatic modulations of the surface potential caused by increasing oxygen depletion. This was further corroborated by experiments in which the apparent roughness tracked in NC-AFM could be correlated with changes in the surface charge distribution that were controlled by applying a bias voltage to the sample. Based on these findings, it is suggested that careful selection of preparation procedures combined with application of an electric field may be used to tune the properties of thin films grown on perovskite substrates.application of an electric field may be used to tune the properties of thin films grown on perovskite substrates.

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

3:40pm **AS-MoA8 In-situ Characterisation of Graphene using combined XPS and Raman Spectroscopy: Removal of Polymer Residue by Ar Gas Cluster Ion Beams*,* *Barry Brennan,*** National Physical Laboratory, UK*; P. Mack,* Thermo Fisher Scientific, UK*; A. Centeno, A. Zurutuza,* Graphenea, Spain*; A.J. Pollard,* National Physical Laboratory, UK

The transfer of chemical vapour deposition grown 2D materials to a relevant substrate material typically involves deposition of a thin polymer layer, usually PMMA, as a handle to transport the 2D material, which is then dissolved in solvent. Any polymer residue is then typically further reduced in a thermal annealing step, designed to break down the polymer chain and remove it from the surface. However, this is rarely fully effective, with trace PMMA residue usually detected. This can then affect the electrical and physical properties of the 2D layer, and prevent consistency in the final material. Recently, a number of mechanisms have been explored to further improve the quality of the transferred layer, from introducing further solvent and annealing steps, to the use of plasmas, and argon gas cluster ion beams (GCIB), to remove any remaining residue. In this study, we explore in detail the use of size selected argon GCIBs to clean polymer residue from a CVD-grown graphene surface. Due to the distribution of the charge applied to the cluster over the individual argon atoms, the energy per atom can be tuned to <0.5 eV/atom, significantly below the bond strength of the graphene, but sufficiently energetic to remove polymeric material.

In order to characterise this, a combination of techniques are needed to thoroughly confirm the removal of polymer material, as well as show there is no impact to the underlying graphene. Ideally these techniques would be in-situ and confocal in nature in order to prevent modifications to the sample surface after cleaning, as well as provide confidence in the measurements. To this end, in this study we used the Thermo Scientific Nexsa X-Ray Photoelectron Spectrometer (XPS) system which allowed us to carry out correlative XPS, REELS and Raman spectrometry in-situ from the same area of a graphene sample during GCIB cleaning. This meant we could examine changes in the chemical composition of the graphene surface as polymer material was removed, while monitoring changes in the Raman spectra to determine whether any defects were being generated in the graphene during the cleaning process. The changes in the sample were further probed using 3D time of flight secondary ion mass spectrometry (ToF-SIMS) imaging, to clearly show the removal of polymer materials during GCIB cleaning, while leaving the underlying graphene layer intact. Through the combination of these measurements, we are able to determine that by keeping the energy per argon atom less than 1 eV, we can prevent the introduction of defects to the graphene layer, as well as significantly decrease the level of contamination present on the graphene surface.

4:00pm **AS-MoA9 Topography-corrected TOF-SIMS Chemical Imaging of Chip Interconnect Surfaces*,* *Conor Thomas*,** *B. Singh, R. Wang,* IBM Systems Division

Next generation computing systems are driving increasingly complex packaging architectures and interconnection techniques to meet higher performance and bandwidth requirements at smaller feature sizes. First-level packaging techniques that incorporate controlled collapse chip connections (C4) in flip-chip applications have become critical to enable near-future microelectronics packaging. Conventional C4 technology uses solder bumps for off-chip interconnections after back end of line wafer fabrication. Solder-based flip-chip technology is currently the industry standard with a proven track record of performance, reliability, and ease of manufacturing at low-cost. However, increasing I/O requirements are pushing the limits of interconnection pitch scalability below 50µm, resulting in a higher spatial density of solder bumps and reduction in solder volume per bump.

The surface cleanliness of fine-pitch solder bumps before chip attachment plays an important role in the solder wetting and reliability of the chip-package interconnect structure. In both flip-chip mass reflow and thermo-compression bonding techniques, the solder bump surfaces go through several assembly steps before chip join and are exposed to potential sources of contamination. Unfortunately, the solder bump surfaces are challenging to study by traditional surface characterization techniques like x-ray photoelectron spectroscopy, Auger electron spectroscopy, and secondary ion mass spectrometry due to the relatively small size of the bumps, the mixed conducting and insulating environments of the sample, and the high curvature of the bumps, respectively. These challenges have only been exacerbated by the decreasing size of the bumps.

Here we describe a new approach to characterize modern solder bumps using a time-of-flight secondary ion mass spectrometer (TOF-SIMS) with an atomic force microscope (AFM) integrated in the same vacuum chamber. We can correlate high spatial resolution TOF-SIMS images with AFM topography images to generate topography-corrected chemical images. With this method we can chemically and spatially characterize the contaminants on solder bump surfaces. This method will be compared with results from Auger electron spectroscopy, our standard method of characterizing solder bump surfaces. We will discuss the important considerations for TOF-SIMS imaging of these highly curved surfaces and approaches to correlate images taken by TOF-SIMS and AFM.

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[1] **NSTD Student Award Finalist**

4:20pm **AS-MoA10 Combining the Benefits of GCIB-ToF-SIMS, MALDI-FTICR-MS and LC-MS/MS for Location specific Lipid Identification in Planarian Flatworm Tissue Sections***, **Tina Angerer**,* University of Washington*; D. Velickovic, C. Nicora, C.R. Anderton,* Pacific Northwest National Laboratory*; D.J. Graham, L.J. Gamble,* University of Washington

Phagocata gracilis are planarian, non-parasitic flatworms. Planarians are best known for their fascinating regenerative abilities, requiring a complex interplay of a wide range of molecules. The regeneration process and the molecules involved are still poorly understood. Most notably there is a lack of lipid and fatty acid data, a diverse group of molecules fulfilling numerous functions such as energy storage and cell signaling.

To gain a better understanding of the lipidomic landscape in planarians we analyzed positive and negative ions from longitudinal sections of *P. gracialis* with MALDI-FTICR-MS and ToF-SIMS along with homogenized whole worm extracts with LC-MS/MS.

Imaging MALDI-FTICR-MS (15T, Bruker Solarix) provides location specific (50 µm/pixel), ultra-high mass resolution (R≈250,000 @m/z=400) and ultra-high accuracy (<1ppm) lipid data capable of distinguishing intact lipid species of similar exact mass and showing their distribution in the tissue. The drawbacks for this technique are that the spatial resolution is too low to clearly identify features within the worm and its low fragmentation rate. While beneficial for molecular peak intensities, the lack of fragments does not allow for specific lipid assignments with structural information (e.g. lipid headgroup and both fatty acid chains identified).

Imaging GCIB-ToF-SIMS (J105, Ionoptika) generates high mass accuracy (< 5ppm), cell/organ-specific data (3 µm/pixel) consisting of intact lipids, lipid fragments and fatty acids. The moderate mass resolution (R≈10,000@m/z=700) is sufficient to resolve most lipid species. Mass peaks consisting of more than one species are indicated by broad and/or asymmetric peaks with poor mass accuracy. However co-localizing fragments can add confidence for the assignment of overlapping species, provide us with structural information and allow for unambiguous identification of resolved peaks.

LC-MS/MS (Thermo Velos Pro Orbitrap) separates different lipid species prior to fragmentation so, in contrast to SIMS, the observed lipid fragments are guaranteed to stem from the analyzed species. The drawback with this technique is that it provides no location specific information. Similar to SIMS, lipids with similar mass are not separated leading to mixed fragments in the MS/MS data. Comparing LC-MS/MS to SIMS data shows that the same lipid fragment species are present in both spectra.

This work demonstrates that only by correlating all 3 techniques can we get highly accurate, high mass, high spatial resolution, structural and location specific lipid information. Together this data provides detailed information about all major structures and organs within planarians.

Biomaterial Interfaces Division
Room 101B - Session BI+AS+IPF+MN-MoA

Advanced Imaging and Structure Determination of Biomaterials Research

Moderators: Dan Graham, University of Washington, Axel Rosenhahn, Ruhr-University Bochum, Germany

1:20pm **BI+AS+IPF+MN-MoA1 NMR Relaxometry as a Medical Diagnostic***,* ***Michael J. Cima***, Massachusetts Institute of Technology **INVITED**

This talk will describe the diagnostic capabilities of magnetic resonance imaging (MRI) when brought to the patient bedside. Rather than imaging, NMR can be used for important chemical/physiologic diagnostic endpoints. Two will be discussed here; quantifying fluid overload and measurement of hypoxia within tumors. Assessment of intra- and extra-vascular volume is integral in managing patients with heart, liver, and kidney disease as volume status is closely linked to mortality. Commonly used determinants of volume status, such as physical exam and ultrasonography, lack sensitivity and specificity and require expertise in clinical practice. This talk reports on nuclear magnetic resonance (NMR) methods to a portable and clinically useful device. A clinical study with hemodialysis patients and age-matched healthy controls was performed at MGH. The T2 relaxation times of study participants' legs were quantified at multiple time points with both a 1.5T clinical MRI scanner and a custom 0.27T single-voxel MR sensor. The results showed that first sign of fluid overload is an increase in the relative fraction of extracellular fluid in the muscle. The relaxation time of the extracellular fluid in the muscle eventually increases after more fluid is accumulated. Importantly, these MR findings occur before signs of edema are detectable on physical exam. Solid tumors are often hypoxic and characterized by an extreme lack of oxygen. Tumor hypoxia imparts significant negative outcomes for patients but is highly variable within cancer types and patient populations. Many of these poor clinical outcomes can be tied to hypoxic-induced radiotherapy resistance. Resistance to radiotherapy in hypoxic regions can be overcome by increasing the dose delivered but exposure limitations of healthy tissue and organs must be considered. The lack of a viable quantitative clinical oxygen measurement method prevents safe dose escalation in these patient populations. Here we report on a silicone-based quantitative oxygen sensor. The MRI contrast of this material depends on dissolved oxygen. Thus, the material functions as a first of its kind solid-state contrast agent. The sensor leverages the existing MRI hardware, which is part of the current clinical work flow, to map tumor oxygen content. This information can then be integrated into the dose planning process clinicians currently conduct to selectively and safely boost dose to low oxygen tumor subvolumes. This sensor is approved by the institutional review board at Dana Farber Cancer Center for a clinical trial in patients locally advanced cervical cancer.

2:00pm **BI+AS+IPF+MN-MoA3 Direct Observation of Cell Signaling Proteins Interacting with a Model Cell Membrane by Sum Frequency Generation Vibrational Spectroscopy***, T.W. Golbek,* Oregon State University*; T. Weidner,* Aarhus University, Denmark*; C.P. Johnson,* ***Joe Baio***, Oregon State University

Proteins that contain C2 domains are involved in a variety of biological processes including encoding of sound, cell signaling, and cell membrane repair. Of particular importance is the interface activity of the C-terminal C2F domain of otoferlin due to the pathological mutations known to significantly disrupt the protein's lipid membrane interface binding activity, resulting in hearing loss. Therefore, there is a critical need to define the geometry and positions of functionally important sites and structures at the otoferlin-lipid membrane interface. Here we describe the first *in situ* probe of the protein structure of otoferlin's C2F domain interacting with a cell membrane surface. To identify this protein's structure at the lipid interface we applied sum frequency generation (SFG) vibrational spectroscopy and coupled it with simulated SFG spectra to observe and quantify the otoferlin C2F domain interacting with model lipid membranes. A model cell membrane was built with equal amounts of phosphoserine (PS) and phosphocholine (PC). SFG studies that examined the ordering of the lipids that make up the model membrane, demonstrate that lipid fusion occurs after docking of the otoferlin C2F domain via the observation of a 62% increase in amplitude from the SFG signal near 2075 cm^{-1} assigned to specific groups within the model membrane. This increase is related to lipid ordering caused by the docking interaction of the otoferlin C2F domain. SFG spectra taken from the amide I region contain peaks near 1621 cm^{-1} and 1672 cm^{-1} related to the C2F domains beta-sandwich secondary structure, thus, indicating that the domain binds in a specific orientation. By mapping the simulated SFG spectra to the experimentally collect SFG spectra, we found the C2F domain of otoferlin orients 32° normal to the lipid surface. This information allows us to map what portion of the domain directly interacts with the lipid membrane. Furthermore, we show first experimental view of any C2 domain of otoferlin docked at the membrane interface, thereby, validating SFG as a method to probe C2 domain-membrane interfaces.

2:20pm **BI+AS+IPF+MN-MoA4 Vibrational Sum-frequency Scattering Spectroscopy for the Characterization of Protein Fiber Structures and their Surface Interactions in Biological Environments***,* ***Patrik K. Johansson****, D.G. Castner,* University of Washington

Biological processes are typically regulated by interactions at the interface of 3D structures, such as the membrane of cells or protein fiber surfaces. Collagen (the most common protein in mammals) forms large fibers that are responsible for the structural integrity of tissues. The structure, organization and interactions of these fibers are furthermore important for the survival, communication, migration, and proliferation of cells.

Investigating protein fiber interactions is challenging, particularly under biological conditions where the fibers exist in a 3D aqueous environment. Many techniques cannot interrogate interfaces buried in the bulk of a solvent and therefore require 2D surface models, while others need extensive purification and sample preparation. These approaches may not capture all key characteristics of the fiber surface structure and interactions in the real sample. However, vibrational sum-frequency scattering (SFS) spectroscopy, with inherent contrast for local molecular ordering, can be utilized towards these important goals.

As a first demonstration, we have applied SFS to protein fibers in aqueous environments, self-assembled from collagen type I. We detected signals from the amide I band and the N-H stretching vibrations, both of which are related to the specific protein backbone structure. Signals from the C-H stretching and bending vibrations were also identified, which are more associated with the side-chains in the fibers. The angular scattering patterns for the backbone (amide I) and side-chain (C-H stretches and bends) signals are different, making the spectra dependent on the angle of detection. While the backbone signals are dominant in the phase-matched direction, the side-chain signals remain high also at large scattering angles. Distinctions in the organizational symmetry and the relative fiber surface contribution to the overall signal are hypothesized as reasons for this observation.

Finally, we are investigating the impact of changes to the environment (e.g. ionic strength, pH, surfactants) on the shape of spectra and scattering patterns for the detected SFS signals. This could yield new insights to the structure and dynamics of collagen fibers in biological settings. The relevance of such investigations is enhanced by the fact that detection of vibrations from the surrounding molecules is a direct observation of their interactions with the collagen fiber surface, which thus can be correlated with the fiber structure. The relative orientations for the detected groups can also be obtained via vibrational SFS polarization analysis, for a deeper understanding of biomolecular interactions in biological processes.

2:40pm **BI+AS+IPF+MN-MoA5 How Proteins Grow Calcium Carbonates – The Mechanism of Vaterite Bioprecipitation Studied at the Molecular Level by Sum Frequency Generation Spectroscopy**, *H. Lu,* Max Planck Institute for Polymer Research, Germany*; S. Roeters,* Aarhus University, Denmark*; H. Lutz, M. Hood, A. Schäfer,* Max Planck Institute for Polymer Research, Germany*; R. Muñoz-Espí,* Universidad de Valencia, Spain*; M. Bonn,* Max Planck Institute for Polymer Research, Germany*; **Tobias Weidner**,* Aarhus University, Denmark

Proteins can act as Nature's engineers at interfaces and manipulate hard tissue growths. Specialized peptides can bind and release specific mineral facets and grow the intricate mineral morphologies found in diatom cell walls, mollusk nacre, but also human teeth and bone. Taking clues from Nature we aim at understanding the mineralization processes at the molecular level and to develop design rules for biogenic nanophase materials. Mineral proteins control the biogenesis of $CaCO_3$ by selectively triggering the growth of calcite, aragonite or vaterite phases. The templating of $CaCO_3$ by proteins must occur predominantly at the protein/$CaCO_3$ interface. Surprisingly, molecular-level insights into the interface during active mineralization have been lacking. Here, we investigate the role of peptide folding and structural flexibility on the mineralization of $CaCO_3$. We discuss the mineral activity of amphiphilic peptides based on glutamic acid and leucine with *ß*-sheet and *α*-helical secondary structures. While both sequences lead to vaterite structures, the *ß*sheets yield free-standing vaterite nanosheet with superior stability and purity. Surface-specific spectroscopy studies and molecular dynamics simulations reveal that the interaction of calcium ions with the peptide monolayer restructures both the peptide backbone and side chains. This restructuring enables effective templating of vaterite by mimicry of the vaterite (001) crystal plane. The approach is universally applicable to mineral peptide engineering. We will discuss how analogous peptide designs can be used to steer the growth not only of calcium carbonates but also calcium oxalates.

3:00pm **BI+AS+IPF+MN-MoA6 ToF-SIMS Imaging of Chemical Modifications in Topographically Challenging Materials**, ***Michael Taylor**, D.J. Graham, L.J. Gamble,* University of Washington

Three-dimensional (3D) porous materials are applied in a variety of areas within materials science[1]. Pores in catalysts provide a high surface reaction area, pores in biofilters facilitate fluid movement for biomolecule capture, and pores in tissue engineered constructs allow for cellular ingress and vascularization. These applications require surface modifications to add specific functionality to their surfaces. The successful functionality of these materials is related to the ability of these modifications to reach all surfaces of the pores. However, it is challenging to characterize these complicated materials and verify the presence and distribution of these surface modifications. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a powerful label-free surface analysis tool that can be used to image the molecular composition of cells, tissues and polymers. Porous 3D materials however, are non-ideal for ToF-SIMS analysis as the technique is highly surface-sensitive, topography on the order of microns can inhibit the ability to produce secondary ions related to surface modifications. To solve this problem we have developed a methodology for filling voids in porous materials to produce a surface where ToF-SIMS imaging may be performed. A embedding process for porous materials with poly(vinyl alcohol)(PVA) is detailed followed by freezing and cryo-sectioning to expose the modified scaffold interior. Here, we demonstrate the versatility of this method by high spatial resolution 3D imaging of a number of surface modifications in PCL poly(caprolactone) scaffolds[2]. Characterisation of fluorocarbon (FC) films deposited using octofluoropropane (C3F8) plasma enhanced chemical vapor deposition (PECVD) will be demonstrated, showing that increased treatment times deposits uniform coatings while shorter treatment results in a gradient distribution of FC throughout the PCL scaffold. Additionally we show data on imaging immobilized/adsorbed proteins within PCL scaffolds. Using this methodology we demonstrate that high spatial resolution label-free 3D imaging of chemical modifications in materials with complex geometries is now possible with ToF-SIMS.

Refs:

(1) Yang, X.-Y.; Chen, L.-H.; Li, Y.; Rooke, J. C.; Sanchez, C.; Su, B.-L. Hierarchically Porous Materials: Synthesis Strategies and Structure Design. *Chem. Soc. Rev.***2017**, *46* (2), 481–558 DOI: 10.1039/C6CS00829A.

(2) Taylor, M. J.; Aitchison, H.; Hawker, M. J.; Mann, M. N.; Fisher, E. R.; Graham, D. J.; Gamble, L. J. Time of Flight Secondary Ion Mass Spectrometry—A Method to Evaluate Plasma-Modified Three-Dimensional Scaffold Chemistry. *Biointerphases***2018**, *13* (3), 03B415 DOI: 10.1116/1.5023005.

3:40pm **BI+AS+IPF+MN-MoA8 Imaging Plant and Plant Growth-Promoting Bacteria Interactions Using Time-of-Flight Secondary Ion Mass Spectrometry**, ***Xiao-Ying Yu**, R. Komorek, Z.H. Zhu, C.J. Jansson,* Pacific Northwest National Laboratory

We present the first imaging and spectra results of plant root interactions with plant growth-promoting bacteria (PGPB) using time-of-flight secondary ion mass spectrometry (ToF-SIMS), showing the successful application of delayed image extraction to study plant biology. Compared to MALDI (Matrix Assisted Laser Desorption Ionization), an imaging mass spectrometry technique widely used in plant studies,[1] SIMS is less destructive and provides submicrometer spatial mapping of molecular species of importance in metabolic processes. *Brachypodium distachyon* (Brachypodium), a genomics model for bioenergy and native grasses, is used due to its small diploid genome, close phylogenetic links to other grass species, relative ease of genetic transformation, short life cycle, small stature, and simple growth requirements.[2] Plant growth-promoting bacteria (PGPB) such as *Pseudomonas* and *Arthrobacter* were introduced to Brachypodium roots prior to analysis, and their potential effect on root extrusion was studied using ToF-SIMS imaging. Specifically, delayed image extraction was used in data acquisition. This approach was chosen to obtain high mass and high spatial resolutions.[3] Excellent SIMS imaging gives topographical description of the root surface with and without PGPB interactions. Distinctive characteristic peaks are observed, indicating compositional changes with and without PGPB introduction to the root surface beside visible surface morphological variations. Our initial results demonstrate that ToF-SIMS is a promising imaging mass spectrometry tool to study plant biology and root-microbe interactions and provide molecular-level insight at the biointerface with high spatial resolution.

References:

[1] D Sturtevant *et al.*, Three-dimensional visualization of membrane phospholipid distributions in Arabidopsis thaliana seeds: A spatial perspective of molecular heterogeneity, Biochimica et Biophysica Acta (2017),**1862**(2), 268-81.

[2] T Girin *et al.*, Brachypodium: a promising hub between model species and cereals, J. Experimental Botany (2014),**65**(19), 5683-96.

[3] QP Vanbellingen *et al.*, Time-of-flight secondary ion mass spectrometry imaging of biological samples with delayed extraction for high mass and high spatial resolutions, Rapid Comm. Mass Spectrom. (2015), **29** (13), 1187-95.

4:00pm **BI+AS+IPF+MN-MoA9 Imaging of Cells and Tissues with Helium Ion Microscopy**, *J.A. Notte, D. Wei, **Chuong Huynh**,* Carl Zeiss Microscopy, LLC

Both optical and electron microscopy are well established techniques in the life sciences with established protocols for imaging and sample preparation. However the newly developed helium ion microscope has some unique advantages, and is gaining a reputation for providing insightful, easy to interpret images over a wide range of biological samples and bio-materials. This presentation serves as both an introduction to this novel technique and a review of recent results.

Because helium ions do not suffer appreciably from diffraction effects, they can be focused to a sub-nanometer probe, providing nanometer scale image resolution with a depth of focus that is well suited to complex surfaces and structures. As helium ions interact with the sample, they provide an abundance of secondary electrons that convey surface-specific and topographical information. Distinctly different from the conventional (gallium) focused ion beams, helium ions do not significantly damage the sample from the sputtering process. And importantly, helium ion microscopy is not affected by charging artifacts when imaging insulating materials, even glass slides, so there is no need for metal over-coating which would otherwise obscure finer details.

Example images will include a pancreatic cell membrane showing the pores and cilia present on their natural surfaces. Other examples will show the complex structure of the principal cell and intercalated cells of the collecting duct of a rat kidney. Other imaging results from diverse fields include stony corals, collagen networks, bone minerals, stereocilia, otoconia, actin filaments, and cryptococcus neoformans. False colorized images of the multi-ciliated epithelial trachea of an adult mouse and T4-phages will also be presented. Finally, new results will be shown from the SIMS spectrometer which provides elemental and isotopic information, and can be the basis for true colorizaton.

In this talk, an emphasis will be placed on the physics principles that enable these imaging results. The selected examples serve to demonstrate the breadth of results that can be attained with this relatively new technique.

4:20pm **BI+AS+IPF+MN-MoA10 Quantitative Analysis of Electrolytes in Microliter-size Blood Drops Congealed via HemaDrop™ using Ion Beam Analysis and SIMNRA***, H. Thinakaran, S.R. Narayan, J.M. Day,* ***Nicole Herbots****, F.J. Ark, B. Wilkens, M. Mangus, R.J. Culbertson,* Arizona State University

Accurate analysis of microliter blood samples can improve medical testing and forensics. Most critically ill patients suffer from hospital-acquired anemia due to the large volume currently required for blood diagnostic tests: 7 mL per vial.

Prior attempts by Theranos to analyze microliter-sized blood droplets in liquid form exhibit systematic errors greater than 10%, higher than the acceptable medical threshold.

This research investigates the accuracy of Ion Beam Analysis (IBA) performed on microliter-sized blood droplets congealed into Homogenous Thin Solid Films (HTSFs) using HemaDrop™, a new patent-pending technique using hyper-hydrophilic coatings to condense fluids into a uniform solid state with a smooth surface.

Prior to IBA analysis, the solidification of blood droplets into HTSF's is observed with optical microscopy and compared to conventional Dried Blood Spots (DBS). DBS exhibit phase separation between platelets and serum, with non-uniform, rough surfaces. Conversely, blood droplets solidified on HemaDrop™-coated surfaces are uniform and smooth, with little phase separation.

Next, quantitative compositional analysis using IBA is performed on µL blood drops solidified on HemaDrop™ coatings and is compared to results on DBS. HTSFs congealed on HemaDrop™-coated surfaces yield well-defined 2 MeV RBS spectra where individual species and electrolytes (C, N, O, Na, K, Ca, Cl, Fe) can be identified, while none can be distinguished on DBS.

The damage curve method [1] extracts elemental composition while accounting for possible IBA damage. Several consecutive spectra are taken on the sample, and RBS yields are interpolated to their original concentrations.

IBA simulations with the software SIMNRA enable comparison between RBS data and simulations, resulting in elemental composition accurate within 1%. Blood electrolyte compositions via SIMNRA are obtained on successive IBA spectra taken on different areas of the thin solid films and on different HTSFs congealed from the same blood. Relative error analysis between different HTSF samples establishes whether reproducibility within 10% can be achieved.

HemaDrop™ reliably creates stable, uniform, thin solid films to measure blood composition from µL-volume drops based on comparative IBA results and optical observations. Measurements of elemental composition of HTSF of blood samples are accurate and reproducible. HemaDrop allows for analysis in vacuo from µL of blood, greatly expanding the range of techniques that can be applied to identify elements and molecules (e.g., antibiotics, proteins).

[1] *Int & US Patent Pending, 2016, 2017

Spectroscopic Ellipsometry Focus Topic
Room 202A - Session EL+EM-MoA

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches

Moderators: Vanya DarakchievaStefan Zollner, New Mexico State University,

1:20pm **EL+EM-MoA1 The Physics of Low Symmetry Metal Oxides with Special Attention to Phonons, Plasmons and Excitons and their Potential for Uses in Power Electronics and Quantum Technologies***,* ***Mathias Schubert****,* University of Nebraska - Lincoln, Linköping University, Sweden, Leibniz Institute for Polymer Research, Dresden, Germany*; A. Mock, R. Korlacki, S. Knight,* University of Nebraska - Lincoln*; V. Darakchieva,* Linköping University, Sweden*; B. Monemar,* Linköping University, Sweden, Tokyo University of Agriculture and Tech., Japan*; H. Murakami, Y. Kumagai,* Tokyo University of Agriculture and Technology, Japan*; K. Goto,* Tokyo University of Agriculture and Technology, Tamura Corporation, Japan*; M. Higashiwaki,* National Institute of Information and Communications Technology, Japan **INVITED**

We discuss analysis of the dielectric function tensor for monoclinic metal oxides. We derive the dispersions of transverse, longitudinal and plasmon coupled modes in gallium oxide [M. Schubert et al., Phys. Rev. B 93, 125209 (1-18) (2016); Editors' Suggestion], the Lyddane-Sachs-Teller relation for monoclinic and triclinic semiconductors [M. Schubert, Phys. Rev. Lett. 117, 215502 (2016)], the identification of transverse and longitudinal phonons in scintillator material cadmium tungstate [A. Mock, M. Schubert et al., Phys. Rev. B 95, 165202 (1-15) (2017)], the band-to-band transitions and excitons and their eigenvectors in gallia [A. Mock, M. Schubert et al., Phys. Rev. B 96, 245205 (1-12) (2017)], the effective electron mass tensor measurement using the optical Hall effect in gallium oxide [S. Knight, A. Mock, M. Schubert et al., Appl. Phys. Lett. 112, 012103 (2018); Editors' Pick], the temperature dependence of band-to-band transitions energies in gallium oxide [A. Mock, M. Schubert et al., Appl. Phys. Lett. 112, 041905 (2018)], and the dielectric and inverse dielectric tensor analysis method for transverse and longitudinal phonon mode dispersion characterization in high-power laser material yttrium silicon oxide [A. Mock, M. Schubert et al., Phys. Rev. B, 97 165203 (1-17) (2018)].

2:00pm **EL+EM-MoA3 Mueller Matrix Spectroscopic Ellipsometry Based Scatterometry of Nanowire Gate-All-Around (GAA) Transistor Structures***, M. Korde,* ***Alain C. Diebold****,* SUNY Polytechnic Institute

One of the most difficult measurement challenges facing semiconductor research and development is determining the feature dimensions and shape for complicated 3D structures. GAA transistors are fabricated from fins etched from a $Si/Si_{1-x}Ge_x/Si/\ Si_{1-x}Ge_x/Si$.. multilayer.(1, 2) At one point in the fabrication process, the nanowires used in GAA transistors have the nanowire transistor structures suspended between the source and drain. Considering the close spacing of neighboring transistors, measuring the nanowires is a significant challenge. In this talk, we present simulations aimed at understanding the sensitivity to changes in feature shape and dimension for the structures used to fabricate GAA transistors. Simulations of the multi-layer fins shown a clear sensitivity to fin shape and Si layer thickness which is enhanced by the use of the full Mueller Matrix capability vs traditional spectroscopic ellipsometry.

1. Optical measurement of feature dimensions and shapes by scatterometry, A.C. Diebold, A. Antonelli, N. Keller, APL Mat., (2018), in press.
2. Muller matrix spectroscopic ellipsometry based scatterometry simulations of Si and $Si/Si_xGe_{1-x}/Si/Si_xGe_{1-x}/Si$ fins for sub 7-nm node gate-all-around transistor metrology, S. Dey, N. Keller, M. Korde, and Alain C. Diebold, SPIE, Metrology, Inspection, and Process Control for Microlithography XXXII, SPIE Advanced Lithography, San Jose, Feb 25-Mar. 1, 2018. To be published in conference proceedings.

2:20pm **EL+EM-MoA4 Anomaly in the Optical Constants of Ni near the Curie Temperature***, **Farzin Abadizaman**, S. Zollner,* New Mexico State University

Magnetized Ni demonstrates an anomaly in its optical constants near the Curie temperature (T_c = 627 K). Experiment shows that this anomaly does not depend on the morphology of the sample. To investigate this feature, we have carried out a series of ellipsometry measurements in the energy range of 0.5 to 6.5 eV as a function of temperature from 80 to 800 K in 25 K steps. Furthermore, temperature dependent Mueller Matrix (MM) measurements have been performed on the magnetized Ni at a single energy of 1.97 eV as a series of four runs, up and down, between 300 and 800 K. The MM data of magnetized Ni reveal slight changes in the anisotropic portion of the MM while passing T_c. However, vast changes in the isotropic MM elements are found, indicating that the anomaly is not due to the induced anisotropy of the sample. The anomaly occurs only in the first run when the temperature passes T_c, which suggests that it stems from magnetization. On the other hand, magnetizing the sample again and repeating the experiment do not demonstrate any anomaly as passing T_c, which disproves our previous suggestion. In fact, the anomaly happens only once for each sample, regardless of its morphology.

No observable variation in the out-of-plane grain sizes were found in the XRD data before and after the temperature measurement. This and the fact that the anomaly occurs for a single crystalline sample as well as for a polycrystalline one indicate that it cannot be due to the grain growth. This turned our attention to the surface effects: Several experiments have been conducted to investigatehow the surface of sample changes around T_c and how cleaning the surface affects the optical constants of Ni. The authors believe that the anomaly around T_c originates from the surface changes. Yet the question of why it occurs near T_c is still open. The same series of experiments have been performed on cobalt and the results are compared to Ni.

2:40pm **EL+EM-MoA5 Phonon Confinement and Excitonic Absorption in the Optical Properties of ZnO Films***, **Nuwanjula Samarasingha**, S. Zollner,* New Mexico State University*; D. Pal, A. Mathur, A. Singh, R. Singh, S. Chattopadhyay,* Indian Institute of Technology Indore, India

Wide band gap materials like ZnO, which have drawn much attention for optoelectronic devices, have a large excitonic binding energy of 60 meV at room temperature. These excitons directly influence the dielectric function (**ε**) of ZnO. Hence investigation of excitonic absorption on the optical properties is very important. Wurtzite type ZnO shows three excitonic peaks in the ordinary dielectric function which are directly related to the electronic band structure. Due to the spin orbit and crystal field splitting the top valence band of ZnO is split into three sub bands . The corresponding free exciton transitions between these three valence bands and the lowest conduction band are denoted by A, C, and B. We also observe an exciton-phonon complex.

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

According to the UV ellipsometry data the real and imaginary parts of **ε** in thin ZnO films on Si are much smaller than in bulk ZnO. We find that the excitonic enhancement decreases monotonically with decreasing film thickness. A similar behavior can be seen for ZnO films on SiO_2 as a function of thickness. The impact of this excitonic absorption on the **ε** was described by Tanguy [1]. We will fit our ellipsometric spectra by describing the dielectric function of ZnO using the Tanguy model. We will investigate the dependence of the excitonic Tanguy parameters on film thickness and substrate material.

Wurtzite type ZnO has 12 phonon branches, 9 optical and 3 acoustic modes. Among these 9 optical modes, only $1A_1$ and $1E_1$ polar phonon modes are IR active. According to the IR ellipsometry data these IR active phonon mode frequencies of ZnO films are consistent with bulk ZnO. We find a small redshift and increasing broadening with decreasing ZnO film thickness on a Si substrate. We will analyze the thickness dependence of the phonon oscillator strength of ZnO films on Si and SiO_2 substrates-.

Reference:

[1] C. Tanguy, Phys. Rev. Lett. **75**, 4090 (1995).

Supported by NSF (DMR - 1505172).

3:00pm **EL+EM-MoA6 High Aspect Ratio Etch Tilt Detection with Full 4x4 Mueller Matrix Spectroscopic Ellipsometry and Its Application to 3DNAND Channel Hole Etch Process and Chamber Monitoring***, P. Ong,* Micron Semiconductor Asia Pte. Ltd., Singapore*; **Shilin Ng**,* Nanometrics Incorporated*; G.B. Chu,* Micron Semiconductor Asia Pte. Ltd., Singapore*; P. Murphy,* Nanometrics Incorporated*; L.C. Liong, W. Fu,* Micron Semiconductor Asia Pte. Ltd., Singapore*; Y. Wen,* Nanometrics Incorporated*; L.W. Ho,* Micron Semiconductor Asia Pte. Ltd., Singapore

Full 4x4 Mueller Matrix Spectroscopic Ellipsometry (MMSE)[1] is a widely-used technique for measuring cross-sectional profile, critical dimensions (CD) and material thicknesses of repeating structures created as part of microelectronic device manufacturing processes. In this paper, it will be shown that its application can be extended to measuring asymmetries in such structures with off-diagonal Mueller Matrix Elements[2]. These asymmetries, such as tilt of etched holes, and lines or trenches, are typically caused by inhomogeneity in the etch plasma sheath at the wafer edge. This paper will focus on one of the most important use-cases: tilt of high aspect ratio (HAR) etched 3D-NAND channel holes. Full 4x4 MMSE can be used to provide fast, accurate, non-destructive measurements of the channel hole tilt, both in direction and magnitude.

Furthermore, in contrast to CD and thickness measurements which are typically done in metrology test keys, this tilt measurement is in-die and on-device. This allows us to characterize the tilt at all locations on the wafer edge, as well as the variation in tilt as the wafer edge is approached. In addition, we also show how the measurements can be used to monitor the condition of the etch chamber for equipment control and/or to trigger preventive chamber maintenance.

3:40pm **EL+EM-MoA8 Ultra-High-Speed Spectroscopic Ellipsometry and its Applications***, **Gai Chin**,* ULVAC Inc., Japan

As a comprehensive manufacturer of metrology tools and deposition tools, ULVAC developed an innovative high-speed spectroscopic ellipsometer for some thin-film deposition applications, such as PVD, CVD, ALD and others.

This novel spectroscopic ellipsometry can measure the thickness and optical constants of thin films at a dramatically fast speed. Its data acquisition time is as short as 10ms. It does not require any active components for polarization-control, such as a rotating compensator or an electro-optical modulator. The Fourier analysis of channeled spectrum obtained from the spectrometer allows determining the four spectroscopic ellipsometry parameters of the samples simultaneously.

It created great opportunities for new applications of the spectroscopic ellipsometry in which the compactness, the simplicity and the rapid response are extremely important. It can be integrated into the deposition tool and successfully measured thin films in-situ to realize the Advanced Process Control (APC). Obviously, those from PVD, CVD and ALD are some promising applications for this novel spectroscopic ellipsometry.

This paper describes the principle, system configuration and creative efforts on developing a series of high-speed spectroscopic ellipsometers. Some of its new applications will be also introduced, such as the PVD, CVD, ALD, EUV, OLED, MEMS and some measurement data of thin films from the semiconductor, flat panel display and other industries.

4:00pm **EL+EM-MoA9 Use of Ellipsometry to Monitor Implant Damage in Methane Plasma Implant***, **Nicholas Bateman**,* Varian Semiconductor Equipment, Applied Materials

The Applied Materials PLAD tool consists of an inductively couple plasma source and a pulsed direct current (DC) bias coupled to a platen upon which a wafer is e-chucked. This tool architecture enables high throughput for high dose implants. Unlike a standard beamline implant, which will not lead to any deposition on the wafer, the plasma implant process directly exposes the wafer to the plasma leading to both deposition and implant damage. Standard industrial metrologies like Thermawave [1] are sensitive only to the implant damage. Process control could be enhanced if both the implant damage and the deposition thickness could be monitored online.

Ellipsometry is extensively used in the semiconductor industry to measure and monitor film thickness and optical properties [2]. It would be the ideal industrial technique to measure the deposition left by a plasma implant process, but has not been used to evaluate the damage caused by ion implant.

This work presents the development of an ellipsometry model that can be used to simultaneously monitor the deposited layer thickness and the implant damage caused by a methane plasma implant. The dispersion function for the deposited layer was determined by fitting multi-angle, broad wavelength ellipsometry data for different process times and bias conditions. The extracted thickness of the damage layer is shown to be well correlated to Thermawave across a wide range of process parameters, and through an extended 'marathon' test. As the implant voltage is reduced to zero the model trends continuously to match the results of a 'deposition only' ellipsometry model that matches SEM thickness measurements.

These results suggest that for plasma doping applications, ellipsometry can be used to monitor both implant damage and deposition simultaneously to allow improved process control.

References:

[1] J Opsal, US Patent 5,074,669, Method and apparatus for evaluating ion implant dosage levels in semiconductors (1989)

[2] DE Aspnes, Journal of Vacuum Science & Technology A, **31**, 058502 (2013)

4:20pm **EL+EM-MoA10 Study of the Thickness-dependent Optical Constants of Metallic Thin Films based on Ellipsometry and Reflectivity***,* ***Jiamin Liu****, H. Jiang, S.Y. Liu,* Huazhong University of Science and Technology, China

Metallic thin films have been widely used in various plasmonic and nanophotonic applications, such as bio-chemical sensors, meta-materials and nanolasers, benefiting by their size-dependent optical constants which are different from that of bulk materials. Considering that the performances of these films are sensitive to their thicknesses and optical constants, it is highly desirable to precisely characterize the thicknesses and the optical constants of such thin films for better applications.

In this work, a synergic analysis method based on ellipsometric parameters and reflectivity has been proposed, which enables the simultaneous determination of both the thickness and the optical constants for the metallic thin film. Both the ellipsometric parameters, including the amplitude ratio tan(ψ) and the phase difference Δ between p- and s-components, as well as the reflectivity are acquired using one ellipsometer. The proposed method consists of a point-by-point synergic regression analysis on the reflectivity and the ellipsometric parameters as well as an oscillator-parametrization regression analysis on the ellipsometric parameters. The former analysis allows for the accurate determination of the thickness of metallic thin films, while the latter enables the acquisition of the optical constants. Both virtual and practical experiments of measuring a series of Cu thin films deposited on Si substrates have been sequentially carried out for demonstration. The results clearly show the coupling effect between the thickness and optical constants of these samples. And by comparing with the thicknessses reported by AFM and TEM, the validity and the accuracy of the proposed method have been verified. Further analysis on the optical constants of Cu thin films has been carried out using the oscillator-parametrization we proposed, in which the thickness dependency of the Drude term, the plasma energy and the relaxation time has also been analyzed.

Electronic Materials and Photonics Division
Room 101A - Session EM+AM+NS+PS-MoA

Atomic Layer Processing: Selective-Area Patterning (Assembly/Deposition/Etching)

Moderators: Michael Filler, Georgia Institute of Technology, Jessica Hilton, RHK Technology

1:20pm **EM+AM+NS+PS-MoA1 Area-Selective Deposition of Crystalline Perovskites***, E. Lin,* ***Brennan Coffey****, Z. Zhang, P.Y. Chen, B. Edmondson, J.G. Ekerdt,* University of Texas at Austin

Epitaxial growth of crystalline perovskites enables opportunities in integrating perovskite properties into electronic and photonic devices. Pattern definition is a necessary step in many device applications and definition through etching can be problematic with titanium-based perovskites. We report a process to grow the perovskite film into the final patterned-dimensions through area-selective atomic layer deposition (ALD) followed by epitaxial regrowth from a crystalline substrate to form a single crystal perovskite film. Epitaxial barium titanate (BTO) films can be grown by ALD on strontium titanate (STO(001)) and STO(001)/Si(001) substrates. The substrates are coated with 40 nm of polystyrene (PS) and 185- and 264-nm UV light projected through a shadow mask is used to crosslink the PS under a N_2 atmosphere. The unexposed PS is stripped using toluene to expose the STO surface. Amorphous BTO films are deposited by ALD at 225 °C on the PS-patterned STO(001) surfaces. The low temperature process prevents the degradation of the PS layer. The PS mask is subsequently removed with an oxygen plasma exposure step. Atomic force microscopy and scanning electron microscopy after BTO growth and crosslinked-PS removal demonstrate high fidelity pattern transfer in the BTO films. Reflective high-energy electron diffraction and x-ray diffraction show that the film crystallizes after annealing the sample in vacuum at ≥ 750 °C, with oxygen partial pressure of 1×10^{-6} Torr. Film orientation as a function of annealing temperature is established with transmission electron and piezoresponse force microscopy.

1:40pm **EM+AM+NS+PS-MoA2 A Dry NF_3/NH_3 Plasma Clean for Removing Si Native Oxide and Leaving a Smooth Si Surface***,* ***Christopher Ahles****, J.Y. Choi,* University of California, San Diego*; A.C. Kummel,* University of California at San Diego

As devices are scaled to sub 5nm, it is critical to prepare clean and atomically flat surfaces. The traditional aqueous HF clean for removal of native Si oxide suffers from an inevitable air exposure resulting in re-oxidation of the Si surface as well as carbon contamination. The Siconi™ process is a dry clean which utilizes a low temperature (<30C) NF_3/NH_3 based plasma to selectively etch the native oxide layer on Si without etching the underlying Si layer. However the Siconi™ process leaves behind a $(NH_4)_2SiF_6$ salt which must be removed in a subsequent anneal. In this work we present a dry clean which eliminates $(NH_4)_2SiF_6$ salt formation and provides a surface which is just as flat as with the traditional aqueous HF clean.

The silicon surface following removal of the native oxide with an NF_3/NH_3 plasma was studied using X-Ray Photoelectron Spectroscopy (XPS) for elemental analysis as well as Atomic Force Microscopy (AFM) for surface roughness measurements. It was found that when the silicon substrate is held at 65-70C during the etching no $(NH_4)_2SiF_6$ salt formation is observed. The NF_3:NH_3 ratio was found to be a critical parameter for controlling the surface roughness, with the surface roughness decreasing with decreasing NF_3:NH_3 ratios. A NF_3:NH_3 ratio of 1:5 gave a Si surface with an RMS roughness of 3.4nm while a NF_3:NH_3 ratio of 1:10 gave a Si surface with an RMS roughness of 1.9nm. Further decreasing the NF_3:NH_3 ratio is expected to provide an even smoother surface, and experiments towards this end are ongoing. The plasma time was also optimized, and it was found that exposure to the NF_3/NH_3 plasma for 10 seconds and 1 minute resulted in essentially no removal of the native oxide, while exposure for 2 minutes resulted in complete removal of the native oxide. For comparison, Si surfaces cleaned with aqueous HF in our laboratory typically have ~10% oxygen and ~10% carbon contamination, while after cleaning with a NF_3/NH_3 plasma with NF_3:NH_3 = 1:10 for 2 minutes at 70C there was 3% O, 0% C, 4% F and 4% N impurities. Additionally, all of the silicon was in an oxidation state of 0 which means that there was no $(NH_4)_2SiF_6$ salt formation since this salt has silicon in an oxidation state of +4. To validate the applicability of this process, a molybdenum silicide film was deposited via atomic layer deposition (ALD) on dry-cleaned Si as well as on HF cleaned Si. The RMS roughness of the ALD $MoSi_x$ film on the dry-cleaned Si was 2.26nm while on the HF cleaned Si the RMS roughness was 2.78nm. This shows that the dry clean developed in this study is capable of producing cleaner and smoother Si surfaces than the traditional aqueous HF clean.

2:00pm **EM+AM+NS+PS-MoA3 Probing Strategies for Selective Deposition that Exploit Competitive Interactions***,* ***James Engstrom****,* Cornell University **INVITED**

Selective thin film processes, including atomic layer deposition, have the potential to enable next-generation manufacturing and patterning at the 5 nm node and beyond, with direct applications in the nanofabrication of functional layers such as gate dielectrics, metal contacts, and capping/barrier layers. Well-known for its ability to deposit atomically thin films with Å-scale precision along the growth direction and conformally over complex 3D substrates, atomic layer deposition (ALD) has emerged as a key nanomanufacturing process. In this regard, the range and scope of ALD-based applications and capabilities can be substantially extended by also controlling the in-plane growth—a timely and significant development that can be realized *via* area-selective deposition processes that depend on the chemical composition of the underlying surface. In this presentation we will review the approaches that have been taken to achieve area-selective ALD, and we shall highlight both the strengths and shortcomings of these approaches. We will also discuss our efforts to achieve selective deposition that exploit competitive interactions—these interactions can occur both on the surface(s) where the film is, or is not, being deposited, and in the gas phase. In our approach we couple well controlled experiments that involve *in situ* surface analysis using techniques such as X-ray photoelectron spectroscopy and high level quantum chemistry calculations of specific and non-specific binding of molecules to target surfaces. We find that this combination of techniques is capable of shedding considerable light on deposition processes that are both potentially fast and leave no trace of their use in guiding thin film deposition to those areas where growth is desired.

2:40pm **EM+AM+NS+PS-MoA5 The Interconnect Resistivity Bottleneck*, Daniel Gall*,** *T. Zhou, E. Milosevic,* Rensselaer Polytechnic Institute*; P.Y. Zheng,* Micron Technology

The effective resistivity of conventional Cu interconnect lines increases by more than two orders of magnitude as their width is decreased from 30 to 6 nm. The resulting increase in signal delay and energy consumption limits downscaling of integrated circuits. This presentation will discuss the search for the most conductive metal solutions for narrow interconnect lines, focusing on three key aspects. (i) Electron surface scattering: In situ transport measurements on epitaxial Cu(001) layers with various monolayer cap-layers demonstrate specular electron surface scattering when the local surface density of states at the Fermi level is negligible, resulting in a considerable copper resistivity reduction. (ii) Alternative metals: The resistivity scaling at reduced dimensions is measured using epitaxial metal layers (Cu, Ag, W, Ta, Ru, Mo, Ni) and directly compared to results from classical transport models using first-principles electronic structure calculations. Multiple elemental metals are expected to be more conductive than Cu for polycrystalline lines <10 nm. (iii) Confined transport model: First-principles non-equilibrium transport simulations in combination with measurements of the resistivity vs roughness and dimensionality are used to develop a new model that accurately accounts for electron surface scattering in quantum-confined 1-D and 2-D conductors. This model will replace semiclassical models that fail to predict the resistivity <10 nm.

3:00pm **EM+AM+NS+PS-MoA6 Sub 0.3 micrometer Copper Patterns Etched with a Plasma-Based Process and Pattern Dependent Electromigration Failure Mechanism*, Yue Kuo,*** Texas A&M University

Copper (Cu) is a popular interconnect material for high density ICs, large area TFT LCDs, and many advanced electronic and optical devices. Since Cu does not form volatile products under the conventional plasma etching condition, the only available method in preparing fine lines is the chemical mechanical polishing (CMP), i.e., the single or dual damascene, method. The author's group has invented a new plasm-based Cu etching method that has a high rate at room temperature (1). This method has been successfully demonstrated in defining submicron lines for IC chips as well as being used in the large area TFT LCDs (2). However, this are few papers on defining the sub 0.5 micrometer Cu line using this new etch method. The lifetime of the plasma-etch Cu line on the flat and stepped surfaces has been studied with the electromigration method (3,4). However, the pattern size effect is rarely discussed.

In this talk, the author will discuss the process that can be used to prepare sub 0.3 micron dimension Cu patterns. The success of this process is due to the simultaneous Cu conversion reaction and sidewall passivation. In addition, the failure mechanism of the plasma-etched Cu line over a large range of line widths, i.e., from 1.5 to 30 micrometers, will be examined based on the electromigration test result. In summary, Cu lines prepared from the plasma-based process can be reliably applied in the many nano electronic and photonic products.

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3:40pm **EM+AM+NS+PS-MoA8 The Effect of Metal Diffusion on Contacts to Semiconducting Chalcogenides: Examples for 2D and 3D Materials*, Suzanne E. Mohney,*** *K.A. Cooley, M. Abraham, A.C. Domask, H. Simchi, L. Kerstetter, C. Lawrence, T.N. Walter,* The Pennsylvania State University **INVITED**

We review our recent studies of contacts to a variety of chalcogenide semiconductors, including few-layered molybdenum disulfide and tungsten diselenide, as well as the phase-change material germanium telluride. In some cases, diffusion of a transition metal into the semiconductor has been correlated with an especially low contact resistance. For example, annealing silver contacts on field effect transistors fabricated from few-layered molybdenum disulfide resulted in a reduction in contact resistance by a factor of 4–5 to 0.2–0.7 kOhm-µm, while the ON/OFF current of the device remained high. Diffusion of silver into molybdenum disulfide was confirmed by secondary ion mass spectrometry. On the other hand, nickel appears to be even more soluble in molybdenum disulfide (as observed by Auger electron spectroscopy), but annealing nickel contacts resulted in an increase in resistance. For the phase-change material germanium telluride, incorporation of iron seems to play a role in achieving a low contact resistance of 0.004 Ohm-mm in annealed Au/Fe/Sn/*p*-GeTe contacts. Diffusion of iron into germanium telluride at a low but detectable level was found beneath a narrow-gap tin telluride interfacial reaction product using energy dispersive spectroscopy in the scanning transmission electron microscope. Using only iron or tin without the other did not result in such a low contact resistance. The influence of iron on the electronic properties of germanium telluride is now under study. Besides diffusion of metals into the semiconductor, we also present cases of reactive contacts to germanium telluride, whereby the contact resistance is greatly increased by interfacial reactions that led to the formation of a new phase (especially nickel tellurides and platinum tellurides). Finally, we consider the influence of surface diffusion on quasi van der Waals epitaxy of metals on layered transition metal dichalcogenides.

4:20pm **EM+AM+NS+PS-MoA10 TiN_x and TaN_x Films via Low-T Thermal ALD using Anhydrous N_2H_4*, Steven Wolf*,** *M. Breeden, M. Kavrik,* University of California at San Diego*; D. Alvarez, J. Spiegelman,* RASIRC*; M. Naik,* Applied Materials*; A.C. Kummel,* University of California at San Diego

For device back end of line processing, there is a need to deposit conformal barrier layers on high aspect ratio 3D architectures via low-T ALD. Titanium nitride (TiN) and tantalum nitride (TaN) have been studied as diffusion barriers to WF_6 during W metal fill and to Cu, as Cu can readily diffuse, causing device reliability issues. Organometallic-grown films are required when Cu is present to prevent etching, however, metal halide precursors are preferred for gate stack applications as films typically contain lower levels of carbon and oxygen contamination; this has been correlated with improved film conductivity. This work aims to deposit thermal ALD titanium nitride and tantalum nitride utilizing anhydrous N_2H_4 at lower temperatures than previously reported with NH_3 while still maintaining good film properties.

In this study, low temperature thermal ALD TiN_x from anhydrous N_2H_4 vs. NH_3 and $TiCl_4$ was performed on degreased and UHV annealed SiO_2/Si substrates at temperatures of 300°C and 400°C. The deposited films were studied using x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). TaN_x films were grown at 150°C utilizing N_2H_4 and tris(diethylamido) (*tert*butylimido)tantalum (TBTDET) and characterized similarly. In addition, the resistance of air-exposed ultra-thin films was measured using a 4-point probe technique. Resistivities were estimated from thicknesses obtained from cross-sectional scanning electron microscopy (SEM) images. First, saturation dosing was performed to determine optimal half-cycle pulses of $TiCl_4$ and N_2H_4. After TiN_x ALD cycles, AFM imaging showed uniform deposition with sub-nanometer RMS surface roughness. The corrected and normalized XPS showed near stoichiometric Ti_3N_4 with low O and C and ~10% Cl. There was approximately 2x more O and C and 50% more Cl in NH_3 grown films at 400ºC. N_2H_4 films exhibited lower resistivities (359 vs. 555 µohm-cm), attributed to this lower contamination and likely better nucleation density. For TaN_x films, XPS of 15 cycles ALD TaN_x films resulted in 9% O and 4% C and had a Ta/N ratio of 4/5. Analysis on the Ta 4d peaks confirmed nucleation after the initial exposure of TBTDET (Si-O-Ta formation) based on the Ta 4d 5/2 peak BE of ~231.5 eV. A chemical shift to 229 eV was observed upon forming Ta-N bonds. Resistance measurements indicated insulating films consistent with the formation of Ta_3N_5. In summary, N_2H_4 grown TiN_x films showed lower resistivities with fewer impurities. The anhydrous N_2H_4 chemistry was extended to an organometallic Ta precursor, in which nearly stoichiometric films were deposited with low contamination at a modest substrate temperature of 150ºC.

Magnetic Interfaces and Nanostructures Division
Room 201A - Session MI+2D+EM+NS-MoA

IoT Session: Symposium on new Magnetic Materials, Devices and Concepts for the Information Society

Moderator: Hendrik Ohldag, SLAC National Accelerator Laboratory

1:20pm **MI+2D+EM+NS-MoA1 "ZOOMING in on Data Storage and the Superb HDD"*, Roger Wood,*** Western Digital **INVITED**

Get ready for a wild ride starting with the vast distances of outer space and ending with the tiny distances that separate atoms. For a very different perspective on data storage, each slide in the

presentation looks at things on a scale that is a factor of ten smaller than the previous slide. The

common thread is the technology of information storage. Information storage is what defines human

history and it is the machine-readable data storage developed in the last half-century that provides the

foundation of the modern information age. More than anything, data storage implies magnetic

recording and the hard disk drive. The humble Hard Disk Drive contains such exquisite technologies

and operates at such astounding precision that it almost defies belief. Yet, our industry churns out

these devices by the hundreds of millions and sells them for a few tens of dollars each. Please enjoy

this light-hearted logarithmic romp through storage technology from interstellar space to interatomic

spacings.

(The presentation is based on a talk given at the annual ASME ISPS banquet in Santa Clara, California, in June 2016, while the author was with Western Digital Corporation.)

2:00pm **MI+2D+EM+NS-MoA3 Physics and Applications of Spin-transfer Torques*, Andrew Kent,*** New York University **INVITED**

The magnetization of a magnetic material can be reversed by using electric currents that transport spin angular momentum [1]. This was predicted in magnetic tunnel junctions—two metallic ferromagnetic layers separated by a thin insulating barrier—by John Slonczewski in 1989 and demonstrated experimentally about a decade later. This discovery has had an enormous impact on magnetism research and technology [2], as prior to this the primary means to reorient the magnetization of a magnet was by applying magnetic fields (dating to 1819 and Oersted!). In this talk I will highlight some of the physics and applications enabled by the discovery of spin-transfer torques. This includes recent experiments that create localized spin-wave excitations (magnons droplets) in thin films with uniaxial magnetic anisotropy [3]. Spin-transfer torques also permit study of magnetic analogues of superconductivity, superfluidity and the Josephson effect that promise to increase our understanding of collective quantum effects. They may even enable braiding Majorana fermions [4]. Finally, I will discuss spin-torque switching of perpendicularly magnetized magnetic tunnel junctions [5], the basic device used in spin-transfer torque magnetic random access memories.

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*Work done in collaboration with Dirk Backes, Gabriel Chaves, Daniel Gopman, Christian Hahn, Jinting Hang, Yuming Hung, Ferran Macia, Daniele Pinna, Laura Rehm, Debangsu Roy, Javad Shabani and Volker Sluka at NYU; Georg Wolf, Bartek Kardasz, Steve Watts and Mustafa Pinarbasi at Spin Transfer Technologies Inc.;and Hendrik Ohldag at SSRL

2:40pm **MI+2D+EM+NS-MoA5 Hybrid Magnetic Heterostructures*, Ivan K. Schuller,*** *A. Basaran,* University of California, San Diego*; J. de la Venta,* Colorado State University*; J.G. Ramirez,* Universidad de los Andes, Colombia*; T. Saerbeck,* Institute Laue-Langevin, France*; I. Valmianski,* University of California, San Diego*; X. Batlle,* University of Barcelona, Spain **INVITED**

Hybrid materials allow the engineering of new material properties by creative uses of proximity effects. When two dissimilar materials are in close physical proximity the properties of each one may be radically modified or occasionally a completely new material emerges. In the area of magnetism, controlling the magnetic properties of ferromagnetic thin films without magnetic fields is an on- going challenge with multiple technological implications for low- energy consumption memory and logic devices. Interesting possibilities include ferromagnets in proximity to dissimilar materials such as antiferromagnets or oxides that undergo metal-insulator transitions. The proximity of ferromagnets to antiferromagnets has given rise to the extensively studied Exchange Bias[1].

In a series of recent studies, we have investigated the magnetic properties of different hybrids of ferromagnets (Ni, Co and Fe) and oxides, which undergo metal-insulator and structural phase transitions. Both the static as well as dynamical properties of the ferromagnets are drastically affected. Static properties such as the coercivity, anisotropy and magnetization [2-3] and dynamical properties such as the microwave response are clearly modified by the proximity effect and give raise to interesting perhaps useful properties.

Work supported by US-AFOSR and US-DOE

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3:40pm **MI+2D+EM+NS-MoA8 Organismic Materials and Intelligence*, Shriram Ramanathan,*** Purdue University **INVITED**

Intelligence in the natural world is panspermic to life, ranging from basic survival skills in non-neural organisms to co-operative foraging and complex mating strategies in higher level animals. We ask the question whether such remarkable features can be implemented in the physical world utilizing adaptive matter. We have identified strongly correlated semiconductors, one class of quantum materials as particularly suited for this effort, owing to their remarkable electronic plasticity. One may refer to these systems as organismic materials that display certain well-defined characteristics of living beings. In this presentation, we will present examples from the animal kingdom focusing on intelligence and episodic memory. Then we will discuss recent collaborative studies on correlated oxides demonstrating ancestral intelligence. We will conclude with examples of neural networks that can be designed with quantum materials that can replicate fundamental animal learning traits. The role of defects, strain and orbital occupancy control in design of electronic plasticity will be highlighted.

In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic

Room 202B - Session MM+AS+NS+PC+SS-MoA

X-ray and Electron Spectromicroscopy in Liquids and Gases & Flash Networking Session

Moderator: Piran Kidambi, Vanderbilt University

1:20pm **MM+AS+NS+PC+SS-MoA1 Bridging the Material and Pressure Gap in Synchrotron based Photoelectron in Situ/Operando Studies*, Luca Gregoratti,*** *M. Amati, P. Zeller,* Elettra-Sincrotrone Trieste, Italy **INVITED**

Modelling the real behavior of technologically relevant materials at typical laboratory environmental conditions is a longstanding challenge. Not only classical pressure conditions are generally far from usual industrial environments (pressure gap) but also heterogeneous materials are very different from those often used to simplify the modelling strategies (material gap). For instance to monitor in-situ/operando the lateral distribution of the chemical state of surfaces and interfaces during a catalytic or electrochemical reaction at sub-micron level at environmental conditions as close as possible to the operational ones is of crucial importance to shed light on the running processes. But the possibility to investigate chemical reactions with X-ray photoelectron spectro-microscopies by overcoming material and pressure gaps is still a challenge also for modern experimental setups.

The Escamicroscopy team of Elettra which operates a Scanning Photoemission Microscope (SPEM) has recently developed novel concepts for a new generation of SPEM working under more realistic pressure conditions. The graphene sealed cells, combined for the first time with XPS by A. Kolmakov [1], allow the possibility to investigate systems which require an ambient pressure regime (e.g. liquid/solid interfaces). Despite the huge ongoing progress in the development and performance of these cells several crucial issues are unsolved and will be addressed by this presentation.

Another recent development is an effusive cell for near-ambient pressure SPEM setups where the highest static pressure achievable is around 1 mbar. Samples are encapsulated in a vacuum sealed cell and located behind a 200 µm diameter size pinhole through which the focused X-ray beam illuminates surfaces and photoelectrons reach the high vacuum path towards the electron analyzer [1].

2:00pm **MM+AS+NS+PC+SS-MoA3 Transition Metal Complexes in Aqueous Solutions Characterized by Liquid Jet Ambient Pressure X – ray Photoelectron Spectroscopy***, **Jared Bruce**, J.C. Hemminger,* University of California, Irvine

Transition metals in aqueous solution have been investigated by a multitude of techniques and are a cornerstone of many aspects of chemistry. Recently, the atmospheric chemistry community has begun to shift their attention to iron, manganese and copper containing aqueous solutions due to their propensity to generate hydroxyl radicals at the air/water interface through a Fenton mechanism. Understanding the chemical state of the transition metal present at the air/water interface, in addition to the distribution as a function of depth, would provide critical insight to the active species of hydroxyl generation. Solvation effects have been shown to significantly affect the distribution of small ions as a function of depth from the vacuum/water interface; first through molecular dynamics (MD) simulations then corroborated by liquid – jet X – ray photoelectron spectroscopy (LJ-XPS). Solvation of transition metals in aqueous solution have added complexity compared to small ions because of complexation of ligands and equilibria with the surrounding solvent.

In our work, using both a lab – based LJ - XPS and synchrotron measurements at the Advanced Light Source, we have shown the distribution of chemical states on a model Fenton reagent, $Fe^{2+}_{(aq)}$, change with depth relative to the air/liquid interface. The chemical state is also sensitive to "spectator" ions in the solution. The presence of Cl^- leads to a binding energy shift in the Fe 2p spectra and a change in the distribution as a function of depth. This is also observed in the Cl 2p spectrum where a binding energy shift of 0.3 eV indicates the presence of an inner sphere Cl that follows the distribution change in the Fe 2p spectrum

2:20pm **MM+AS+NS+PC+SS-MoA4 Interfacial Electrochemistry in Liquids Probed with Photoemission Electron Microscopy***, S. Nemsak,* Forschungszentrum Juelich GmbH, Germany*; E. Strelcov,* NIST Center for Nanoscale Science and Technology*; **Tomas Duchon**,* Forschungszentrum Juelich GmbH, Germany*; H.X. Guo,* National Institute of Standards and Technology*; J. Hackl,* Forschungszentrum Juelich GmbH, Germany*; A. Yualev,* NIST Center for Nanoscale Science and Technology*; I. Vlassiouk,* Oak Ridge National Laboratory*; D.N. Mueller, C.M. Schneider,* Forschungszentrum Juelich GmbH, Germany*; A. Kolmakov,* NIST Center for Nanoscale Science and Technology

The use of photoemission spectromicroscopy as a probe of liquid electrolytes has been an elusive goal, motivated by the breadth of information the technique can provide, but hindered by many technical difficulties. Here, we present a universal multichannel array platform employing graphene capping that allows for investigation of interfacial liquid electrochemistry via soft x-ray absorption and photoemission spectromicroscopy. The methodology is demonstrated in the case of copper electroplating from a sulphuric acid solution, that, along with cycles of copper deposition on gold electrodes, reveals hindered nucleation at the electrified graphene membrane evidenced by the presence of stable Cu+ ions.

3:40pm **MM+AS+NS+PC+SS-MoA8 Practical Liquid Cell Microscopy - Opportunities and Challenges***, **Daan Hein Alsem**, K. Karki,* Hummingbird Scientific*; J.T. Mefford, W.C. Chueh,* Stanford University*; N.J. Salmon,* Hummingbird Scientific **INVITED**

Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and synchrotron X-ray microscopy (XRM) are powerful characterization tools and are routinely used to study a wide range of material-systems at the nanoscale. This has generated strong interests in acquiring more reliable quantitative *in-situ* and *operando* measurements in realistic reaction environments, as is possible with liquid environmental cells. This approach has already started to produce new insights on the dynamics and structural changes during electrochemical processes as lithium ion insertion/extraction, dendrite formation, metal nucleation and corrosion. However, practical aspects of replicating representative electrochemical data reminiscent of bulk behavior are still a challenge in these systems.

Here, we will discuss practical aspects of conducting *operando* liquid cell microscopy experiments relating to the typical geometry of these liquid-cell microscopy systems as well as artifacts coming from the microscope during *operando* experiments. We will also present a TEM/SEM/XRM microscopy platform that enables true electroanalytical measurements mimicking bulk behavior of the material system.

The example study shown here is performed using electrochemical cells, which consist of two microfabricated chips sandwiched with transparent SiNx membranes for encapsulating liquid and viewing in the microscope. A newly developed hardware system and specially optimized electrochemistry chips with a custom configuration for working electrode (WE), counter electrode (CE) and reference electrode (RE) allows quantitative measurements of electrochemical processes with details resembling the complete cycle of the bulk. As illustrations, we present cyclic voltammetry (CV) studies of some model compounds such as 01.M $CuSO_4$ and 20 mM $K_3Fe(CN)_6$/20 mM $K_4Fe(CN)_6$ in 0.1M KCl solutions. In the former case, the copper deposition and stripping occurs at the working electrode at distinct redox peaks in liquid cell and the result mimics the bulk electrochemical cells with large electrode areas and larger volume of electrolyte solution. This work highlights the fact that with suitable hardware systems and with knowledge and correction of microscope-induced artifacts, bulk behavior of the electrochemical processes can be both observed and measured quantitatively.

4:20pm **MM+AS+NS+PC+SS-MoA10 Observation of Electric Double Layer under Graphene by Scanning Electron Microscopy***, **Hongxuan Guo**, A. Yulaev, E. Strelcov,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; A. Tselev,* CICECO and Department of Physics, University of Aveiro,Portugal*; A. Kolmakov,* National Institute of Standards and Technology

The formation of the electric double layer is a fundamental phenomenon occurring at electrified solid-liquid electrolyte interfaces and which has a key importance for energy devices, chemical engineering and biomedical applications. The structure and composition of electric double layer can be accessed using optical methods [1], and more recently with X-ray spectroscopy [2, 3], as well as scanning probe microscopy[4].

In this presentation, we demonstrate the feasibility of *in-situ* scanning electron microscopy to observe the changes in electric double layer in different electrolytes upon polarization. We designed an electrochemical liquid cell with electron transparent electrode made of bilayer graphene.[5,6]. We monitored the changes in secondary electron yield from the graphene-liquid interface upon electrolyte polarization. We found that the normalized SEM image contrast is linear with the applied bias voltage and is related to the concentration and distribution of the ions at the interface. The analysis of SEM videos provide insight on long term kinetics of ionic moieties in electrolyte during polarization. This experimental methodology will be helpful for understanding the structure, property, and dynamics of the electric double layer at solid -electrolyte interfaces.

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Materials and Processes for Quantum Computing Focus Topic
Room 203A - Session MP+AM+EM+NS-MoA
Systems and Devices for Quantum Computing II

Moderator: Josh Mutus, Google Inc

1:20pm **MP+AM+EM+NS-MoA1 Quantum Engineering of Superconducting Qubits***, William Oliver,* MIT Lincoln Laboratory **INVITED**

Superconducting qubits are coherent artificial atoms assembled from electrical circuit elements and microwave optical components. Their lithographic scalability, compatibility with microwave control, and operability at nanosecond time scales all converge to make the superconducting qubit a highly attractive candidate for the constituent logical elements of a quantum information processor. Over the past decade, spectacular improvement in the manufacturing and control of these devices has moved superconducting qubits from the realm of scientific curiosity to the threshold of technical reality. In this talk, we review this progress and our own work at MIT that are creating a future of engineered quantum systems.

2:00pm **MP+AM+EM+NS-MoA3 The Quantum Socket: A Wiring Method for Superconducting Quantum Computing***, **Matteo Mariantoni**,* University of Waterloo, Canada **INVITED**

I will provide a brief introduction to the main technological and scientific challenges to be faced in order to build a practical quantum computer, with emphasis on the case of superconducting quantum computing. I will then delve into a detailed explanation of a method to address the wiring of a two-dimensional array of superconducting quantum bit (qubits): The quantum socket [1]. Next, I will show how the quantum socket can be extended to a medium-scale quantum computer and how it can help mitigate coherent leakage errors due to qubits interacting with spurious cavity modes [2]. I will then show thermocompression bonding technology [3], a method that allows us to further protect qubits from the environment. In particular, I will propose a new qubit design based on our experimental implementation of thermocompression bonded chips, where vacuum gap capacitors are used to reduce dissipation due to so-called two-level state defects in amorphous dielectrics, which are the insulators presently use in our qubits.

[1] J.H. Béjanin, T.G. McConkey, J.R. Rinehart, J.D. Bateman, C.T. Earnest, C.H. McRae, Y. Rohanizadegan, *D. Shiri*, B. Penava, P. Breul, S. Royak, M. Zapatka, A.G. Fowler, and **M. Mariantoni**, Three-Dimensional Wiring for Extensible Quantum Computing: The Quantum Socket, Phys. Rev. Applied **6**, 044010 (2016)

[2] T.G. McConkey, J.H. Béjanin, C.T. Earnest, C.R.H. McRae, Z. Pagel, J.R. Rinehart, **M. Mariantoni**, Mitigating Coherent Leakage of Superconducting Qubits in a Large-Scale Quantum Socket, Quantum Sci. Technol. 10.1088/2058-9565/aabd41 (2018)

[3] C.R.H. McRae, J. H. Béjanin, Z. Pagel, A.O. Abdallah, T.G. McConkey, C.T. Earnest, J.R. Rinehart, and **M. Mariantoni**, Thermocompression Bonding Technology for Multilayer Superconducting Quantum Circuits, Appl. Phys. Lett. **111**, 123501 (2017)

3:00pm **MP+AM+EM+NS-MoA6 50 Ohm Superconducting Kinetic Inductance Traveling-Wave Amplifier with flexible pump frequency for Four Wave Mixing and Three Wave Mixing***, **Xian Wu**, M. Bal, J. Long, H.S. Ku, R. Lake, D.P. Pappas,* National Institute of Standards and Technology

We developed a 50 Ohm transmission-line based superconducting kinetic inductance traveling-wave (KIT) amplifier using high inductance material NbTiN. The nonlinearity originates from the kinetic inductance of the superconductor and enables amplification. Often, the impedance of the transmission line is significantly higher than the 50 Ohm microwave environment due to the dominance of kinetic inductance over geometric inductance at micron size scales. To address this impedance mismatch, we engineered "fingers" on each side of the original coplanar waveguide KIT [1] to introduce extra capacitance that decreases the impedance to approximately 50 Ohm [2,3]. Those extra "fingers" also function to create a band stop at higher frequency to bend the dispersion relation between wave vector (k) and frequency (f), which allows us to apply the pump frequency within a wide span of a few GHz and achieve several GHz gain bandwidth for chosen pump frequency. Another advantage of this structure is that it significantly reduces the phase velocity, hence shortening the physical length of this device. Gain measurements based on both four wave mixing and three wave mixing will be presented.

[1] Appl. Phys. Lett. **108**, 012601 (2016); https://doi.org/10.1063/1.4937922

[2] Journal of Applied Physics **119**, 083901 (2016); https://doi.org/10.1063/1.4942362

[3] Appl. Phys. Lett. **110**, 152601 (2017); https://doi.org/10.1063/1.4980102

3:40pm **MP+AM+EM+NS-MoA8 Near Term Development of Short Depth Quantum Processors***, J.M. Chow,* IBM Research Division, T.J. Watson Research Center*; **Martin Sandberg**,* IBM, T.J. Watson Research Center **INVITED**

Quantum processors are currently in their infancy though the community is poised to explore bringing them to a state where they can outperform classical computations in relevant application. The challenges that lie ahead are plentiful and touch all aspects of the quantum computer, ranging from finding algorithms to building control software and control hardware as well as engineering and fabricating and testing the quantum hardware. In an effort to accelerate the development of quantum computing IBM launched the IBM Q experience. The Q Experience is a cloud-based platform which allows anyone to get familiar with quantum computing. It allows users to run experiments on actual quantum hardware.

In this talk I will focus on the development and characterization of short depth superconducting quantum hardware. Crosstalk and decoherence are some of the most pressing issues that we face today. Decoherence limits the number of operations that can be performed on the hardware (the depth of the circuit) whereas crosstalk can limit what operations can be performed in parallel on the circuit. The processors featured on the IBM Q experience are based on fixed frequency transmon qubits with a cross-resonance based two qubit gate. For this platform only a very narrow frequency range for the qubits is possible. This leads to problems related to frequency crowding and spurious interactions. Methods for characterizing and addressing both the frequency allocation and characterizing crosstalk will be discussed.

4:20pm **MP+AM+EM+NS-MoA10 Frequency Crowding in Lattices of Transmon Qubits***, S. Rosenblatt, **Jared Hertzberg**, J. Chavez-Garcia, N.T. Bronn, H. Paik, M.O. Sandberg, E. Magesan, J. Smolin, J.B. Yau, V.P. Adiga, M. Brink, J.M. Chow,* IBM, T.J. Watson Research Center

A key goal in quantum computing is to develop scalable fault-tolerant quantum logic circuits. One promising architecture involves lattices of fixed-frequency transmon qubits coupled via cross-resonance gates. Fixed-frequency qubits offer high coherence and the all-microwave gate reduces circuit complexity. To optimize gate performance, excitation energies of neighboring qubits must be similar but non-degenerate. This architecture is thus sensitive to any variation in device parameters affecting transmon frequency. In this talk we will discuss a statistical model for the resulting 'frequency crowding' behavior, and suggest improvements in both architecture design and qubit fabrication in order to achieve scalable circuits with good gate fidelity.

*We acknowledge support from IARPA under Contract No. W911NF-16-0114.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+2D+AS+PC-MoA

SPM - New Imaging and Spectroscopy Methodologies

Moderators: Aubrey Hanbicki, Naval Research Laboratory, Sidney Cohen, Weizmann Institute of Science, Israel

1:20pm **NS+2D+AS+PC-MoA1 A Connection Between Stability of STM Control System and Local Barrier Height: Implications on Imaging and Lithography***, **S.O. Reza Moheimani,*** University of Texas at Dallas **INVITED**

Poor performance of the Scanning Tunneling Microscope (STM) control system may result in tip-sample crash, a prevalent failure in STMs. Since its invention, about thirty-five years ago, few attempts have been made to improve the STM control system. Consequently, nearly all STMs are today operated with experimentally selected fixed-gain PI controllers. Selection of controller gains is often done without much attention to the electromechanical dynamics of the scanning tunneling microscope. Performance of such poorly-tuned controllers is limited and a key contributor to the tip-sample crash.

We perform closed loop system identification on a scanning tunneling microscope and show that the system DC gain is proportional to the square root of Local Barrier Height (LBH), a quantum mechanical property of the sample and/or tip that affects the tunneling current. We demonstrate that during a scan the LBH may undergo significant variations and thus it may adversely affect the closed-loop stability if the controller parameters are fixed. Feedback instabilities increase the risk of tip-sample crash in STMs.

In order to improve the closed loop performance, we estimate the LBH, on the fly, and use this information to adaptively tune the PI controller parameters. Experimental results obtained with the self-tuning PI controller confirm the improved STM performance compared to the conventional fixed gain PI controller. Further experiments confirm effectiveness of the proposed method in extending the tip lifetime by lowering the chance of the tip/sample crash.

2:00pm **NS+2D+AS+PC-MoA3 Distinctive Microstructures in a Complex Polymer Evolve with Time and Composition***, x. Yu,* Worcester Polytechnic Institute*; S. Granados-Focil,* Clark University*; M. Tao, **Nancy Burnham,*** Worcester Polytechnic Institute

The diverse microstructures observed by atomic force microscopy (AFM) in asphalt binder – a complex polymer – suggest complicated intermolecular associations. These microstructures contribute to binders' bulk mechanical properties; therefore, it is essential to understand chemical-microstructural-mechanical relationships for optimal design of binder-related applications, which range from roads to roofs. The US market for asphalt binders in 2019 is predicted to reach 148 million barrels. [1]

Binders annealed at room temperature for over two months showed time-dependent microstructures, which correlate well with room-temperature steric hardening behavior as verified by other researchers using modulated differential scanning calorimetry. Microstructures of the binder films stabilized after different annealing durations, depending on the dimensions of the molecular structures and the complexity of the molecular interactions among the multiple phases in each bitumen. Distinctive microstructures were observed for remixed binders with increasing asphaltene concentrations. Consistency between our observations [2] and other literature suggests that microstructures observed by AFM are probably not just a surface phenomenon.

Furthermore, the complex nature of binder and the various influencing factors often lead to practical challenges in investigation of its microstructures and their chemical origins. Some of the main concerns related to AFM characterization of binders' microstructures, namely the dependence of the microstructures on such factors as sample preparation methods, annealing conditions and durations, and chemical composition, were also addressed in this study.

The above findings provide practical knowledge and deeper insights into the establishment of the complicated chemical-mechanical relationships for asphalt binders that pave the way toward tuned binder performance.

[1] https://www.reportlinker.com/p0158665/US-Asphalt-Industry.html

[2] "Time- and composition-dependent evolution of distinctive microstructures in bitumen." X. Yu, S. Granados-Focil, M. Tao, and N.A. Burnham, Energy Fuels 32, 67-80 (2018).

2:20pm **NS+2D+AS+PC-MoA4 Offering new Characterization Capabilities at the XTIP beamline by Combining Scanning Tunneling Microscopy with Synchrotron Radiation***, **Volker Rose**, H. Chang, M. Fisher, S.W. Hla, N. Shirato,* Argonne National Laboratory

The race is on for chemical x-ray imaging with nanoscale resolution. Specifically, there are currently substantial efforts underway at synchrotron facilities worldwide that aim to combine x-rays with scanning probe microscopy. Recently, substantial progress was made on Argonne's Synchrotron X-ray Scanning Tunneling Microscopy (SX-STM) project. SX-STM enables an entirely new view into the nanoworld by combining the best of two worlds: the exceptional chemical, magnetic, and structural sensitivity of synchrotron x-rays combined with the high spatial resolution of scanning probe microscopy accompanied by its ability to engineer and manipulate surfaces down to the level of single atoms.

To fully exploit the special capabilities of a unique new cryogenic x-ray microscope, XTIP, a dedicated beamline for SX-STM will become available at the Advanced Photon Source in early 2019. To meet the scientific objective of the nanoscience and nanomagnetism communities most effectively, we are going to build a soft x-ray beamline with full polarization control operating over the 500-1600 eV energy range. The dedicated XTIP beamline will provide researchers access to a one-of-a-kind instrument. Among the potential breakthroughs are "designer" materials created from controlled assembly of atoms and molecules, and the emergence of entirely new phenomena in chemistry and physics.

2:40pm **NS+2D+AS+PC-MoA5 Scanning Probe Microscopy Based Spectroscopy Measurement for Nanoscale Chemical Identification***, **Chanmin Su,*** Bruker-Nano, Inc. **INVITED**

Scanning probe microscopy has been instrumental for physical property characterizations at the nanometer scale, primarily for mechanical, electromagnetic and thermal properties. Recent progresses were focused on chemical identification based on mid-IR spectroscopy, pushing FTIR mapping to a resolution at or beyond 10 nm. This presentation will review technology advances in both scanning near field optical microscopy and photothermal based IR spectroscopy. Each of the techniques is discussed and benchmarked by detection limit, spatial resolution and signal to noise ratio, which ultimately determines the chemical mapping efficiencies. We will highlight techniques that address correlative imaging where physical and chemical properties at the same nanoscale location being acquired either concurrently or sequentially. As an example, PeakForce tapping based chemical and physical measurements will be explained in detail with the applications ranging from 2D materials to polymer complexes. The presentation will also highlight major challenges for scanning probe based measurements to be broadly adopted as the premier tool for nanoscale chemical fingerprint mapping.

3:40pm **NS+2D+AS+PC-MoA8 Quantifying Tip-Sample Interactions in Vacuum Using Cantilever-based Sensors: An Analysis***, O.E. Dagdeviren, C. Zhou, E.I. Altman, **Udo D. Schwarz,*** Yale University

To achieve as much quantitative information on a surface as possible, the local measurement of tip-sample interaction potentials has recently gained much popularity in particular under well-defined ultrahigh vacuum conditions, where such measurements can be carried out with great accuracy both in terms of spatial as well as force resolution. To this end, either the oscillation frequency or the oscillation amplitude and phase of the vibrating force-sensing cantilever are recorded as a function of tip-sample distance and subsequently converted into quantitative values for the force or interaction potential. Here, we theoretically and experimentally show that the force law obtained from such data acquired under vacuum conditions using the most commonly applied methods may deviate more than previously assumed from the actual interaction when the oscillation amplitude of the probe is of the order of the decay length of the force near the surface, which may result in a non-negligible error if correct absolute values are of importance [1]. Caused by approximations made in the development of the mathematical reconstruction procedures, the related inaccuracies can be effectively suppressed by using oscillation amplitudes sufficiently larger than the decay length. To facilitate efficient data acquisition, we propose a novel technique that includes modulating the drive amplitude at a constant height from the surface while monitoring the oscillation amplitude and phase.Ultimately, such amplitude sweep-based force spectroscopy enables shorter data acquisition times and increased accuracy for quantitative chemical characterization compared to standard approaches that vary the tip-sample distance. An additional advantage is that since no feedback loop is active while executing the amplitude sweep, the force can be consistently recovered deep into the repulsive regime.

[1] O. E. Dagdeviren et al., Physical Review Applied **9**, 044040 (2018).

4:00pm **NS+2D+AS+PC-MoA9 AFM + Nanoscale Vis-IR Spectroscopy via Photo-induced Force Microscopy***, **Derek Nowak**, T. Albrecht, S. Park,* Molecular Vista

Photo-induced Force Microscopy (PiFM) [1] combines optical spectroscopy and atomic force microscopy (AFM) via illumination of the tip-sample junction with tunable laser light and mechanical detection of forces acting on the tip in response to interaction of light with the sample. With infrared (IR) source, PiFM can map the IR absorption of the sample as a function of IR wavelength and position and achieve nm-scale resolution in displaying the locations of heterogeneous materials on the surface of a sample. Even for samples without active IR absorption band, PiFM can be used to acquire nanoscale mapping based on the dielectric constant of the sample surface; dielectric constant mapping also allows high resolution sub-surface mapping. With tunable visible and near infrared (VisNIR) laser source, PiFM can map exciton resonances with similar spatial resolution even on monolayer samples. Examples from various classes of samples including organic, inorganic, and 2D materials will be presented. We will also present PiFM spectroscopy data that show excellent correlation with bulk FTIR spectra despite the fact that PiFM acquires local chemical information from regions in the range of 10 nm in extent.

[1] D. Nowak et al., Sci. Adv. **2**, e150157 (2016).

Plasma Science and Technology Division
Room 104A - Session PS+PB-MoA

Plasma and Polymers: 'The Legacy of Riccardo d'Agostino and Beyond'

Moderators: Ankur Agarwal, KLA-Tencor, Mohan Sankaran, Case Western Reserve University

1:20pm **PS+PB-MoA1 Foreword/introduction to the session: "Reflections on the Legacy of Riccardo d'Agostino"***, P. Favia,* University of Barii, Italy

In this contribution I will review the career of Prof. d'Agostino and reflect on his scientific achievements, his extensive network in the field of plasma chemistry, plasma processing of materials and applications, and his role as mentor for several generations of M.Sc. students as well as PhD and postdocs.

1:40pm **PS+PB-MoA2 Atmospheric Pressure PE-CVD of Drug-containing Nanometric Capsules***, **Pietro Favia**, C. Lo Porto, A. Treglia,* University of Bari, Italy*; F. Palumbo,* CNR Institute of Nanotechnology NANOTEC, Italy

Plasma Enhanced Chemical Vapor Deposition Processes have been investigated by Riccardo d'Agostino and co-workers, and by many of his colleagues, in the late 80s and early 90s, mainly at low pressure, resulting in a large number of publications on the deposition kinetics and on the applications of coatings of different composition and properties. Many other PE-CVD approaches have been developed since then, and the deposition processes have been or are going to be deeply investigated, following the legacy of Riccardo d'Agostino in this field.

In this talk we present a set of data on the direct PE-CVD of nanometric capsules in the plasma phase resulting from Aerosol Assisted (AA) Atmospheric Pressure (AP) PE-CVD processes fed with Helium (carrier), Ethylene (film precursor) and aerosol droplets of solutions of drugs (nancomicyn, gentamicyn, etc). This approach [1, 2, 3] can lead, in certain conditions, to the deposition of thin coatings directly on the droplets of the aerosol, thus leading to the synthesis of drug-containing nanometric capsules, of potential interest for biomedical applications, e.g., as anti-bacterial surfaces [4].

The influence of various plasma parameters on the AA-AP-PE-CVD processes is discussed, as well as some properties of the coatings.

acknowledgements

The mentorship of Prof. d'Agostino is acknowledged by the authors of this contribution, as well as the recognition of his legacy in the field of plasma processing of materials.

references

1. A. Heyse et al, Plasma Proc. Polym. 8, 965 (2011)
2. Palumbo et al, Plasma Proc. Polym. 12, 1302 (2015)
3. Lo Porto et al, Polym. Chem. 8, 1746 (2017)
4. Sardella et al, *Materials* 2017, 9, 515

2:00pm **PS+PB-MoA3 Ultrathin Metal-Organic Covalent Networks by initiated Plasma Enhanced Chemical Vapor Deposition (iPECVD) for Gas Separation Membranes***, **Karen Gleason**, M. Wang,* MIT*; N.D. Boscher,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; M.C. Creatore, A. Perrotta,* Eindhoven University of Technology, The Netherlands*; K. Heinze,* Johannes Gutenberg-Universität, Mainz, Germany

Metal-Organic Covalent Networks (MOCN) were synthesized as ultrathin (<100 nm), defect-free and mechanically flexible layers by initiated Plasma Enhanced Chemical Vapor Deposition (iPECVD). The low substrate temperature used for iCVD allowed use of thermal sensitive porous poly[1-trimethylsilyl)-1-propene] (PTMSP) as a substrate. Uniform layers were grown over 150 nm diameter substrates and did not delaminate upon mechanical deformation. The resulting robust MOCN/PTMSP composite membranes exhibiting outstanding gas separation performance for multiple pairs of gases. Using zinc (II) meso-tetraphenyl porphphyrin (ZnTPP) as the monomer and tert-butyl peroxide as the initiator, film deposition was achieved at low plasma excitation powers. The nearly unchanged intensity of the Soret bands in the UV-vis spectra confirmed the retention of the 18 pi e- conjugation of the monomer units incorporated into the films. The gas selectivity for the separation of H_2/CH_4 or H_2/N_2 is small (<3) for either the PTMSP base membrane or for thin films of evaporated ZnTPP. However, the gas selectivity for both H_2/CH_4 or H_2/N_2 rises to >500 for the PTMSP/iPECVD ZnTPP composite membrane, exceeding the performance of commercial membranes. Ellipsometric Porosimetry and Density Functional Theory Calculations are consistent with a pore size of ~0.4 nm in the MOCN film. Additionally, iPECVD layers derived from a metal-free porphyrin and from porphyrins containing magnanese (III) and cobalt (III) will be described.

2:20pm **PS+PB-MoA4 Influence of Energetic Conditions on the Plasma Polymerization of Cyclopropylamine in Capacitively Coupled Discharges***, **Lenka Zajickova**, M. Michlicek,* Masaryk University, Czech Republic*; S. Hamaguchi,* Osaka University, Japan

Thin films prepared by plasma polymerization of cyclopropylamine (CPA) in capacitively coupled discharges demonstrated their attractive functional properties as a matrix layer in immunosensors or surface modification of synthetic polymers used for a cell cultivation. These bioapplications required tuning the concentration of amine and other bio-active groups together with the film stability in aqueous media. Since the final plasma polymer composition is influenced by the discharge power and the polymer cross-linking can be modified by ion energy flux towards the growing film the investigation of bulk plasma and plasma-surface interactions with respect to the energetic conditions are necessary for fundamental understanding of the overall process. This work puts together the results on the plasma polymer properties with the plasma diagnostics by mass and ion spectrometry, optical emission spectroscopy and retarding field energy analyzer placed at the substrate position. The experiments are complemented by the molecular dynamic simulations of the film growth.

2:40pm **PS+PB-MoA5 Electrochromic Investigation of PEDOT Film Deposited by Plasma Radicals Assisted Polymerization *via* CVD***, **Bianca Rita Pistillo**, G. Lamblin, J. Polesel-Maris,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; K. Menguelti,* Luxembourg Institute of Science and Technology (LIST)*; D. Arl, D. Lenoble,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Quite recently conducting polymer have been introduced into a broad range of organic electronic devices in place of analogous inorganic semiconductors, owing to their numerous merits as flexibility, low cost and lightweight over their forerunners. Similarly to inorganic material, also conducting polymer display electrochromism. The oxidation or reduction of these films is usually associated with reversible ion insertion and extraction across an electrochromic material/electrolyte interface with complementary electron transfer across the electrochromic material/electrode interface. In the last years, the study and implementation of organic electrochromic materials (OEM) into devices had a tremendous growth also because of their relatively narrow absorption band in displaying diverse and clear colour. [T.T. Steckler et al. J. Am. Chem. Soc. 2014, 136, 1190] There are many interesting applications of OEM such as smart windows, flexible displays, electrochromic fibres, etc. One of the most attractive ones is Poly(3,4-ethylenedioxythiophene) (PEDOT) with its derivatives. PEDOT changes its colour from dark blue/purple, in its reduced state, to light blue, in the oxidised state with very low applied switching potential. Plasma Radicals Assisted Polymerization via Chemical Vapour Deposition (PRAP-CVD) has been developed at Luxembourg Institute of Science and Technology as an efficient alternative to conventional vapour-based processes of conductive thin films as PEDOT. [D. Lenoble, Controlled radical assisited polymerization, Lux. 91934, 2013] This process is based on the concomitant but physically separated injection of low-energy oxidative radical initiators and vaporized monomer species into a reactor where temperature and pressure are finely controlled. [B.R.Pistillo et al. J. Mater. Chem. C 2016, 4, 5617] A few advantages of making the process completely dry include the possibility of processing solvent-sensitive substrates such as paper, overcoming the effects of rinsing on the underlying films in the case of multilayer structures. Moreover, PRAP-CVD allows the deposition of highly conformal coatings, which accurately follows the geometry of the underlying substrate independently from its nature, enlarging the application of PEDOT as OEM. In this work, we present the investigation of electrochromic properties of PRAP-CVD PEDOT films. The behaviour of films was compared with the data in the literature revealing a faster switching time compared to other vapour-based processes reported. The range of switching potential with limited electrochemical degradation of the thin electrochromic film was also investigated by the means of UV-visible spectroelectrochemistry.

3:00pm **PS+PB-MoA6 Initial ZnO Crystallite Formation by Plasma Enhanced ALD***, **Alberto Perrotta**, J. Pilz, A.M. Coclite,* Graz University of Technology, Austria

ZnO is a wide direct bandgap semiconductor, extensively studied as thin film because of its unique optical, electrical, and piezoelectric properties. Its crystalline structure and degree of crystallinity have a crucial impact on the material characteristics and a particular crystallographic texture may be beneficial for gaining optimized piezoelectric properties or enhanced velocities in surface acoustic wave devices. Therefore, the possibility to control the preferred crystallographic orientation in ZnO thin films has been often investigated.

Atomic layer deposition (ALD) offers the possibility to study in detail the growth of ZnO, due to its layer-by-layer nature and sub-nm thickness control. The initial growth of ZnO adopting diethylzinc (DEZ) and water and its impact on the crystallographic texture of the resulting thin films shed light on the growth mechanisms and the influence of the substrate nature on the in-plane and out-of-plane crystal orientations.

However, thin films deposited with plasma enhanced ALD are known to show several differences when compared to thermal ALD. Therefore, for ZnO thin films the growth mechanism and initial crystallite formation may be greatly influenced by the use of plasma. In this contribution, the initial growth of direct plasma ALD ZnO grown on Si (100) is investigated. DEZ and pure oxygen plasma are adopted during the process. The first 20 cycles of growth are analysed using synchrotron light grazing incidence X-ray diffraction (GIXD), X-ray reflectivity (XRR), and spectroscopic ellipsometry (SE). The influence of substrate temperature ranging from 25 °C to 250 °C on the crystal growth and crystal orientation are studied. A closed layer was obtained within 7 cycles as measured by XRR for all the temperature explored, suggesting island growth of the ZnO. However, GIXD showed no crystalline texture forming at this stage. An amorphous intermixed interface between the native SiO_2 and the growing layer was found, with a density in between pure SiO_2 and ZnO. Irrespective of the deposition temperature, the first crystal structure was measured at around 3 nm, with a preferential out-of-plane orientation transiting from (100) at room temperature to (002) at 250 °C. The first crystallographic seeds were found to largely determine the final microstructure of thicker films.

3:40pm **PS+PB-MoA8 On Fluorocarbons and Fish: Creating a Global Impact on Generations of Plasma Chemists***, **Ellen Fisher**,* Colorado State University

Plasma processing represents a powerful approach to modification of a range of substrates with an array of chemistries and morphologies. One of the most useful plasma processing tools is that of plasma polymerization for thin film formation. Arguably, the work of Riccardo d'Agostino and his coworkers over numerous decades, especially in the arena of fluorocarbon film deposition, has significantly enhanced our understanding of plasma polymerization and influenced countless additional studies around the globe. Here, we will detail how d'Agostino's work based in Bari, Italy inspired a range of studies of various fluorocarbon systems that have been performed over more than 2 decades in one laboratory nearly 6000 miles away. Despite the foundational data provided by d'Agostino's early examination of plasma polymerization processes, the remaining paucity of data regarding the fundamental, molecular-level mechanisms that drive fluorocarbon and hydrocarbon plasma polymerization begged further examination. Combining a range of spectroscopy techniques, materials characterization tools, and plasma-surface interface studies has yielded another generation (or two) of insight. This presentation will focus on film deposition studies utilizing multidimensional substrates (e.g. membranes, scaffolds, nanomaterials), and the connections between d'Agostino's pioneering plasma polymerization work and our more recent studies relevant to a range of value added products, including blood-contacting devices, sensors, tissue engineering, and separation technologies.

4:00pm **PS+PB-MoA9 DIRECT and Remote Surface Functionalization using Atmospheric Pressure Dielectric Barrier Discharges***, **Francesco Fracassi**,* University of Bari, Institute of Nanotechnology (NANOTEC), NRC, Italy, Italia*; F. Fanelli,* Institute of Nanotechnology (NANOTEC), NRC, Italy, Italia*; V. Armenise, A. Uricchio, R. d'Agostino,* University of Bari, Italy, Italia

The utilization of atmospheric pressure dielectric barrier discharges (DBDs) for the surface modification of materials is a very interesting and actual topic. In recent years, efforts have been directed toward the development of a large variety of processes which exploit different DBD configurations and electrode geometries. This contribution describes DBD-based deposition and treatment processes which are potentially of interest also for environmental applications. The processes are performed on polyurethane (PU) foams, i.e., three-dimensional porous substrates which can be quite uniformly surface functionalized by DBDs, since, under suitable experimental conditions, the discharge ignites both outside the foam and throughout its entire porous structure. Three experimental strategies are utilized: i) direct treatment and deposition in parallel plate DBD; ii) direct aerosol-assisted deposition in parallel plate DBD; iii) remote deposition of thin films containing carboxylic acid groups with DBD jet.

The direct treatment is performed by feeding the DBD with He-O_2 mixtures in order to form carboxyl groups on the polyurethane surface. The treated foams are able to adsorb heavy metals from water solutions and can be regenerated (release of adsorbed heavy metals) through immersion in concentrated sodium chloride solution. However, the treated foams suffer ageing in water and, therefore, at the second reuse the amount of adsorbed metals decreases. A water-stable surface containing carboxyl groups is obtained with the DBD jet fed with helium-acrylic acid-ethylene mixtures (remote thin film deposition). No morphological and chemical modifications of the deposits are detected also after 72 h of immersion in water.

When the parallel plate DBD is fed with He-C_3F_6 mixtures, the deposition of fluoropolymer thin films occurs on both the exterior and interior of the foam. The treated foams are superhydrophobic and oleophilic, simultaneously, with potential application for the separation of oil from polluted water, since they selectively adsorb oil, while repelling water.

The direct aerosol-assisted deposition in parallel plate DBD is utilized to prepare hybrid organic-inorganic nanocomposite coatings composed of a hydrocarbon polymer and ZnO or TiO_2 nanoparticles. Under appropriate deposition conditions, it is possible to obtain multifunctional coating characterized by superhydrophobicity, superoleophilicity as well as by the peculiar photocatalytic properties of the utilized nanoparticles. The application of the treated foams for oil-water separation and for the photocatalytic degradation of organic pollutants in water is currently under investigation.

4:20pm **PS+PB-MoA10 Quest for Durable Low-index Optical Coatings: From Plasma Polymerized Fluorocarbons to Hybrid Organic-inorganic and Nanostructured Films***, Martinu, **Jolanta Klemberg-Sapieha**, O. Zabeida,* Ecole Polytechnique de Montreal, Canada

Low (n less than about 1.55@550nm) and ultra-low refractive index materials (n less than 1.38@550nm) are of particular interest in the context of enhanced optical performance of interference filters (IF, including anti-reflective coatings). In addition, for many years now, there has been a lot of effort to develop such low and ultra-low index films with multifunctional characteristics making them suitable for the applications of IF on plastic and flexible substrates. This includes a necessity to better understand and optimize the thermo-mechanical properties (hardness, Young's modulus, adhesion, thermal expansion coefficient), surface energy (hydrophobicity), and possibly provide complementary functionalities (color, electrical conductivity, etc.). This presentation provides an overview of the progress in the field outlined above, starting with the work performed jointly with Professor Riccardo d'Agostino. In the first part, we describe the main optical, mechanical and dielectric characteristics of plasma polymerized fluorocarbons and related metal-doped plasma polymers. In the second part, we introduce hybrid organic-inorganic (SiOCH) materials that are shown to combine high mechanical resistance of ceramics with high elasticity of polymers. We demonstrate, that the refractive index of such films can vary from 1.50 to 1.53, while the extinction coefficient is kept below 10-4. At the same time, the hardness-to-Young's modulus ratio, H/E, is substantially increased (to 0.16) compared to 0.08 for pure SiO2), a result that is well correlated with the increased resistance to crack formation and propagation. Such layers, incorporated in multilayer structures on plastic substrates, provide significantly enhanced optical and mechanical stability in environments involving large temperature and humidity excursions. In the third part, we explore the characteristics of a new category of hybrid SiOCH thin films prepared by glancing angle deposition (GLAD) using electron beam evaporation of SiO2, in the presence of an organo-silicone precursor. The resulting layers are shown to exhibit n as low as 1.2, high elastic rebound and high hydrophobicity, and better mechanical properties than their inorganic counterparts. Their performance is discussed in terms of their anisotropy assessed by the nanostructure-based spectroscopic ellipsometry model. Finally, we demonstrate successful implementation of the ultra-low index material in a complete IF stack.

Advanced Surface Engineering Division

Room 202C - Session SE-MoA

New Challenges and Opportunities in Surface Engineering

Moderators: Robert Franz, Montanuniversität Leoben, Austria, Jianliang Lin, Southwest Research Institute

1:20pm **SE-MoA1 From Passive to Active Optical Coatings - Challenges and Opportunities for Pulsed Plasma Deposition Processes***, **Ludvik Martinu**,* Ecole Polytechnique de Montreal, Canada **INVITED**

Optical coating (OC) applications represent a multibillion dollar market worldwide; they range from antireflective (AR) coatings found in most optical components and low emissivity windows in buildings and automobiles to narrowband optical interference filters used in telecommunications. As the range of applications of OCs continuously broadens and extremely attractive market opportunities arise, it is becoming increasingly important to develop new nanostructured thin film materials with specific multifunctional properties. Further progress in this fast evolving field is strongly stimulated by a simultaneous action of two forces: a) the "pulling force" represented by the economic, technological and societal needs, including sustainable development, and b) the "pushing force" related to the curiosity-driven nanotechnology combining new design concepts of materials and devices, fabrication processes and innovative characterization tools, where the only limitation frequently appears to be our imagination.

This presentation will describe a h olistic approach to OCs based on a broad and in depth knowledge of the interplay between the design, material, process and performance assessment with respect to specific applications and coating system durability in demanding environments. It will review the progress and future opportunities for the use of discrete, graded, and nanostructurally-controlled architectures benefiting from the nanomaterials' meta-structures, advanced deposition techniques including high power impulse magnetron sputtering (HiPIMS) and tailored plasma- and ion-surface interactions, as well as complex systems implementing active (smart, tunable) materials.

Tomorrow's trends will be illustrated by examples from different fields of applications ranging from passive hybrid elastic OC for ophthalmic lenses, hard protective OC for displays, and optical interference filters for gravitational waves detection to active OC and advanced glazings for energy saving using smart windows, active color-shifting security and authentication devices, and smart radiators with self-tuned emissivity for the thermal management in satellites.

2:00pm **SE-MoA3 Anomalous Orientation-dependent Slip during Uniaxial Compression of TaC Crystals***, M. Chen,* ETH Zurich, Switzerland*; D.G. Sangiovanni,* Ruhr-University Bochum, Germany and Linköping University, Sweden*; A. Aleman, H. Zaid,* University of California at Los Angeles*; J.M. Wheeler,* ETH Zurich, Switzerland*; G. Po, **Suneel Kodambaka**,* University of California at Los Angeles

Binary carbides of group IV-VI transition-metals are hard, stiff, and high-melting solids with excellent high-temperature mechanical and chemical stabilities and good resistance to wear, ablation, and corrosion. Recent studies suggest that cubic B1-structured group IV and V transition-metal carbides, ZrC and TaC, are not intrinsically brittle and that they can exhibit plasticity under compression. Here, we present our results obtained using a combination of in situ scanning-electron-microscopy-based uniaxial micro-compression tests and ab initio molecular dynamics simulations conducted on TaC crystals, along with density functional theory calculations and finite-element based modeling of discrete dislocation and crack dynamics. We find that the room-temperature mechanical behavior of TaC is highly anisotropic and the operating slip systems are not necessarily those expected based on their Schmid factor. We find that the room-temperature mechanical behavior of TaC is highly anisotropic with yield strengths as high as ~17 GPa for <100> and as low as ~5 GPa for <310> crystals. Interestingly, the operating slip systems are not necessarily those expected based on their Schmid factor. We attribute the observed behavior to the normal component of the applied forces (in the direction perpendicular to the slip), whose magnitude varies with the slip plane and the crystal orientation. This anomalous slip results in the activation of {110}<110> slip systems during uniaxial compression of <100>, <110>, and <310> crystals and {111}<110> slip systems in <111> crystals and leads to the observed anisotropy in yield strengths. We suggest that similar behavior should be expected in this class of materials.

2:20pm **SE-MoA4 Selectable Phase Formation in Al-based Transition Metal Nitride Films by Controlling Al^+ Subplantation depth during HIPIMS Deposition***, **Grzegorz Greczynski**,* Linköping University, Sweden*; S. Mraz, M. Hans,* RWTH Aachen University*; J. Lu, L. Hultman,* Linköping University, Sweden*; J.M. Schneider,* RWTH Aachen University, Germany

Alloying with Al is a common strategy to improve thermal and chemical stability of transition metal nitride (TMN) coatings deposited by magnetron sputtering. The solubility of Al in rock-salt-structure TMNs is, however, limited which presents a great challenge to increase Al concentration substantially, while avoiding precipitation of thermodynamically-favored wurtzite-AlN phase (*w*-AlN), which is detrimental to mechanical properties.

We present a novel thin film deposition method, which allows for unprecedented control over the phase formation in metastable TMN layers. The technique relies on hybrid high power impulse/dc-magnetron co-sputtering (HIPIMS/DCMS) of elemental targets in Ar/N_2 gas mixture with precise synchronization of the substrate bias pulse to the Al^+-populated portion of the HIPIMS discharge which is superimposed onto a continuous TM neutral flux supplied from a DCMS-operated target. This results in a separation of film-forming species in time and energy domains and enables us to overcome the limitations of the conventional processing where phase formation is to large extent determined by the high adatom mobility and gas-ion-induced mixing, both taking place at the very surface, which drive the system towards thermodynamic equilibrium.

To demonstrate versatility of this technique we grow three series of high-Al-content films, namely $Ti_{0.28}Al_{0.72}N$, $V_{0.26}Al_{0.74}N$, and $Zr_{0.48}Al_{0.52}N$, all as a function of the amplitude of the synchronized bias pulse, which corresponds to varying the incident energy of Al^+ ions $E_{A1}{}^+$. For all materials systems, the crystalline phase content is a very sensitive function of $E_{A1}{}^+$ and can be tuned from completely hexagonal in the limit of low $E_{A1}{}^+$ values ($\lesssim$60 eV) to pure cubic obtained with $E_{A1}{}^+ \gtrsim 250$ eV. A complete transition from hexagonal *w*-AlN to supersaturated cubic NaCl structure is a consequence of the fact that the subplantation depth of Al^+ metal-ions increases with increasing $E_{A1}{}^+$, as supported by Monte Carlo TRIDYN simulations. This innovative synthesis methodology enables unprecedented control over the phase formation and, hence, film properties and opens novel scientific avenues.

2:40pm **SE-MoA5 Metallic-Glass Nanotube Arrays: A Novel Device for Various Applications***, **Jinn P. Chu**, J.K. Chen, C.C. Yu,* National Taiwan University of Science and Technology, Taiwan, Republic of China **INVITED**

A new group of thin film metallic glasses have been known to exhibit properties different from conventional crystalline metal films, though their bulk forms are already well-known for properties such as high strength because of their amorphous structure. We successfully fabricated the first-ever metallic glass nanotubes (MGNTs) on Si by a simple lithography and sputter deposition process for very large-scale integration. Like biological nanostructured surfaces, MGNTs show some surprising water repelling and attracting properties. Nanotubes are 500-750 nm tall and 500-750 nm in diameter, shown in Figure 1 [1]. The MGNT surface becomes hydrophobic, repelling water. By heating and cooling the array, water can be repelled and attached to the surface [1]. There are two examples presented in this talk based on modifications of this scheme. First, after modification of biotin, the array acts as a waveguiding layer for an optical sensor. The MGNT sensor waveguide could readily detect the streptavidin by monitoring the shift. The detection limit of the arrays for streptavidin is estimated to be 25 nM, with a detection time of 10 min. Thus, the arrays may be used as a versatile platform for high-sensitive label-free optical biosensing [2]. Second, the array is prepared on a heating device on Si and, with an applied electric voltage to the heating device underneath, the array surface was heated to generate an extending force from these nanochambers so that the array are functioned as biomimetic artificial suckers for thermally adhesion response in biological systems [3].

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3:40pm **SE-MoA8 Biocompatibility and Antibacterial Behaviors of TaON(porous)/TaN/TaN-Ag/Ta Multi-layered Thin Films***, **Joe. H. Hsieh,*** Ming Chi University of Technology, Taiwan, Republic of China*; C. Li,* National Yang Ming University, Taiwan, Republic of China*; C.C. Hsu,* Ming Chi University of Technology, Taiwan, Republic of China

In this study, a triple-layered thin film structure was designed and fabricated in order to realize porous and tunable TaOxNy thin films with enhanced biocompatibility and antibacterial behavior. In the design of film structure, the top layer was made of porous and tunable TaOxNy. The porous structure was obtained from TaOxNy-Cu (>50 at.%) thin films deposited by reactive sputtering. After the film was annealed by using RTA (1st annealing), the Cu phase was etched away to form TaOxNy network structure. The bottom layer was TaN-Ag (11 at.%) which is used as a Ag source layer. It also provided toughness and hardness. A thin TaN film was inserted between porous TaOxNy layer and solid TaN-Ag layer, and used as Ag diffusion control layer. The function of this layer was to withstand the 1st annealing, then, during the 2nd annealing, to let certain amount of Ag diffusive to the porous TaOxNy layer, and formed Ag nanoparticles. The films fabricated based on this design were studied systematically on their mechanical properties, Ag particle formation, as well as pore size and morphology. Finally, antibacterial property and biocompatibility of these films were studied in terms of O/N ratio, dealloying process, and Ag diffusion control. The relationships among O/N ratio, Ag nanoparticle formation, porosity, and bio-reactions will be discussed and reported systematically.

4:00pm **SE-MoA9 Electrochemically Deposited Coating with Antibacterial Properties against the Spread of Heath Care-associated Infections***, **Nicole Ciacotich,*** Technical University of Denmark, Denmark*; J.B. Rasmussen,* Elplatek A/S, Denmark*; K.N. Kragh,* University of Copenhagen, Denmark*; P. Møller, L. Gram,* Technical University of Denmark, Denmark

Health care-associated infections (HCAIs) are one of the major causes of patient morbidity during hospitalization. Most, if not all, HCAIs are the consequence of proliferation and transmission of pathogenic microorganisms in hospitals, especially in intensive care units. In addition, a range of items and devices, including hospital furniture (bedrails, frames, door handles) are fomites that often have a high load of pathogenic agents.

In a previous study, we developed an electroplated copper-silver alloy as antibacterial coating on stainless steel to minimize adhesion and transfer of pathogenic bacteria on environmental surfaces. We have characterized the electroplated copper-silver alloy in its microstructure, chemical and electrochemical nature and demonstrated a pronounced antibacterial activity.

The purpose of the present study was to evaluate the antibacterial efficacy in a standardized surface adhesion tests against *Staphylococcus aureus* 8325. We determined the influence of chlorine and phosphorus compounds, well-known complexing agents of copper common in hand sweat and surface detergents, by comparing the antibacterial effect of stainless steel, silver, copper and copper-silver alloy. In presence of phosphates and chlorides, the copper-silver coating showed the highest antimicrobial efficacy followed by copper, compared to stainless steel and silver. In absence of chlorides, there was no statistically significant difference among the different metal surfaces.

We also demonstrated that the antibacterial effect of the copper-silver alloy was considerably reduced if the direct contact between surface and bacteria, but not the passage of ions, was prevented. This suggests that the antibacterial action is mainly due to the so-called contact killing mechanism, which is distinctive of metallic copper, rather than the release of copper ions.

Furthermore, we performed confocal microscopy of bacteria on copper-silver coated surfaces using a modified live/dead staining in order to follow over time the bacterial killing front at the surfaces. This demonstrated, as the assays based on counting, a rapid killing spreading upwards in the bacterial biofilm within 30 minutes.

In conclusion, we believe that the electroplated copper-silver coating can be an effective instrument limiting spread of pathogenic microorganisms causing HCAIs in hospitals and intensive care units.

4:20pm **SE-MoA10 Tunable Self-Healing Thermal Barrier Coatings***, S.S. Joshi, **J.J. Gu**, Y.-S. Ho, B.W. Wei, T.Y. Hung, Y.Y. Liu, N.B. Dahotre, S.M. Aouadi,* University of North Texas

Oxide ceramics exhibit a wide spectrum of unique properties, but can suffer from unpredictable and often catastrophic crack propagation and fracture, which limits their use in some applications. One possible solution to overcoming this limitation is to leverage the ability of oxides to repair their inherent flaws and cracks, i.e. to self-heal. The aim of the work is to gain new insights into self-healing mechanisms of a subset of ceramic surfaces, namely thermal barrier coatings, in response to thermal stimuli. TBCs are extensively used to protect metallic blades in gas-turbine engines against harsh operating conditions that include elevated temperatures and corrosive environments. Model systems that were investigated include YSZ-Al2O3-SiC and YSZ-Al2O3-TiC laser processed coatings. The healing process occurs when the carbide phase oxidizes and the resulting oxide flows to the crack site and bonds to the YSZ matrix. The formation of the oxide phase was observed using X-Ray diffraction its formation in the crack site was confirmed using cross-section scanning electron microscopy. The optimum process to create a self-healing composite was determined. Finally, the mechansisms responisble for how the self-healing process impacts deformation and failure resistance as well as corrosion resistance at elevated temperatures was investigated.

Surface Science Division
Room 203C - Session SS+HC-MoA

Theory and Modeling of Surfaces and Reactions

Moderators: Liney Arnadottir, Oregon State University, Petra Reinke, University of Virginia

1:20pm **SS+HC-MoA1 Elucidating the Chemical Nature of Single-Site Catalysts from First Principles***, A.J.R. Hensley,* Washington State University*; A.J. Therrien,* Tufts University*; R. Zhang,* Washington State University*; A.C. Schilling,* Tufts University*; K. Groden,* Washington State University*; E.C.H. Sykes,* Tufts University*; **Jean-Sabin McEwen,*** Washington State University **INVITED**

Automotive catalysis is more complicated than most applications of catalysts, because of the complex and dynamic changes in the exhaust gas environment. The ability to create highly dispersed, single-site catalysts, which are highly efficient and have low cost, is very much desirable [1]. While single atom sites can be created, there is still disagreement over whether the single atom sites are indeed catalytically active or if the observed catalytic activity of single-site catalysts is due to metal nanoparticles either unobserved during initial microscopy studies or formed upon exposure to catalytic conditions [2]. Such disagreements create a crucial need for the development of well-defined single-site catalysts with an accurate theoretical model in order to correctly determine the chemical nature of the catalytically active sites. To this end, we have studied low-temperature CO oxidation on Pt single-site catalysts supported on the “29” Cu surface oxide. The “29” Cu surface oxide is a high coverage chiral structure. Through the use of scanning tunneling microscopy (STM), CO temperature programmed desorption (TPD), and density functional theory (DFT) techniques, we determined that an accurate model for the “29” Cu oxide surface is formed from the growth of a Cu_xO layer formed from 6 fused hexagonal rings above the Cu (111) surface where 5 oxygen adatoms are added at the center of the Cu_xO rings [3, 4]. Furthermore, the state of the Pt single atoms before, during, and after reaction is determined through a combination of theoretical and experimental techniques. It is found that the Pt dosed to the “29” Cu oxide surface forms well dispersed single atom sites which are metallic in nature [5]. During catalysis, CO_2 forms from the combination of an oxygen from the “29” Cu oxide surface with the CO adsorbed on the Pt single atoms.

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2:00pm **SS+HC-MoA3 Unravelling the Complex Features in STM Images of O/Ag(110) System**, ***Takat B. Rawal,*** University of Central Florida; *M. Smerieri,* IMEM-CNR, UOS Genova, Italy; *J. Pal,* University of Genova, Italy; *S. Hong,* Brewton-Parker College; *M. Alatalo,* University of Oulu, Finland; *L. Savio, L. Vattuone,* University of Genova, Italy; *T.S. Rahman,* University of Central Florida; *M. Rocca,* University of Genova, Italy

Elucidating the various structures involving oxygen adsorption on silver surfaces is a key issue in understanding the industrially relevant Ag oxidation process. Recently it was demonstrated that atomic oxygen can cause the extraction of substrate atoms off metal surfaces. In particular for Ag(110), the excavation process takes place already when O_2 is dosed at 175 K leading, at low coverage, to the formation of single Ag vacancies [1], which can serve as reactive sites. Vacancy creation proceeds thereby via the formation of O-Ag-O complexes, which involve a local reconstruction of the surface and ignite the disruption of the Ag substrate. Here, we present details of such processes and of the various structures formed by the O adatoms at very low coverage, for some of which the energetics had already been reported in ref. [2]. To this purpose we performed scanning tunnelling microscopy experiments and density functional theory calculations. A variety of features such as isolated grey dots, sombreros, shallow grey and white structures oriented along [001] and [1-10], grey stripes, and lozenges were identified and assigned to the O adatoms in different configurations. Most of the oxygen ends up either in “zig-zag chain” or in pinned, “lozenge” shaped structures. The former interact strongly with the STM tip and are easily disrupted, giving rise to highly mobile, sombrero shaped, isolated O adatoms. Around 200 K, not only Ag vacancies are mobile with anisotropic migration rates and can merge at larger coverage into complex features, but also the mobile Ag atoms are trapped by O adatoms leading finally to the O-Ag chains oriented along [001] forming the well-known added row reconstruction.

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2:20pm **SS+HC-MoA4 First Principles Investigations on CO_2 Adsorption and Dissociation on $Cu_{cluster}$ / Cu(111) Surfaces: Influence of Co-adsorbed CO Molecule**, ***Allan Abraham Padama,*** University of the Philippines Los Baños, Philippines; *H. Nakanishi, H. Kasai,* National Institute of Technology, Akashi College, Japan; *J.D. Ocon,* University of the Philippines Diliman, Philippines

Cheap Cu surfaces play important role in the synthesis of methanol and in reverse water gas shift reactions, in which, the interaction of the surfaces with carbon dioxide (CO_2) is an important process. Recent developments revealed the stable structures of Cu clusters on Cu(111) ($Cu_{cluster}$ / Cu(111)) that is activated by CO adsorption [Science 351 (6272), 475-478]. Interestingly, it is found that the surface facilitates water dissociation. In connection to these, we see the importance of studying the adsorption and dissociation of CO_2 on this system which could provide additional insights to the use of Cu-based surfaces as catalyst in various reactions.

In this work, we performed first principles calculations based on density functional theory (DFT) to investigate the adsorption and dissociation of CO_2 on $Cu_{cluster}$ / Cu(111), with and without the presence of co-adsorbed CO molecules. We modeled the system with three Cu atoms as cluster, which was experimentally identified as among the stable clusters on the Cu(111). The adsorption energy of CO_2 on $Cu_{cluster}$ / Cu(111) is ~0.25 eV, comparable to the obtained adsorption energy of CO_2 on flat Cu(111). We found that the cluster and the presence of CO do not influence the dissociation of CO_2. An activation energy of ~1.6 eV accompanies the dissociation when it takes near the cluster which is similar to the barrier on pristine Cu(111). The dissociation barriers on the cluster region are ~1.0 – 1.2 eV, lower than on Cu(111), and it appears that co-adsorbed CO molecules do not significantly affect the dissociation process. CO_2 that dissociates directly on the cluster is only accompanied by ~0.6 eV activation barrier, but further diffusion of the adsorbed species away from the cluster increases the barrier. The geometric and electronic properties analyses that support the obtained results will be presented in the symposium.

2:40pm **SS+HC-MoA5 Step-Spacing Distributions Revisited: New Motivations from Curved Crystals and Other Systems**, ***Theodore L. Einstein,*** University of Maryland, College Park

Recent experiments on curved crystals of noble and late transition metals (Ortega and Juurlink groups) have renewed interest in terrace width distributions (TWD) for vicinal surfaces. We first summarize refinements of TWD analysis that are absent from the standard reviews. Rather than by Gaussians, TWDs are better described by a single-parameter distribution with a power-law rise and a Gaussian decay, thereby including effects evident for weak step repulsion: skewness and peak shifts down from the mean spacing. Curved crystals allow analysis of several spacings with the same substrate, so that one can check the scaling with the mean width. This is important since such scaling confirms well-established theory. Failure to scale also can provide significant insights. Complicating factors can include step touching (local double-height steps), oscillatory step interactions mediated by metallic (but not topological) surface states, short-range corrections to the inverse-square step repulsion, and the offset between adjacent layers of almost all surfaces. We discuss how to deal with these issues. Many of the curved-crystal experiments involve in-plane misoriented (zig-zag) steps. There are formulas to describe the stiffness but not yet the strength of the elastic interstep repulsion. Some theory results are available for these orientations; more are needed. Other intriguing results have been reported for spacings of spiral steps around a dislocation.

3:40pm **SS+HC-MoA8 Elucidating Mechanisms of Alkanol Catalysis on $SrTiO_3$ Perovskite Surfaces using Density Functional Theory**, ***Robert Chapleski***, *S. Roy,* University of Tennessee Knoxville

Targeted at understanding observed differences in reaction dynamics for various alkyl alcohols on catalytic $SrTiO_3$ surfaces, we describe the results of our computational study of isopropanol adsorption and catalysis on $SrTiO_3$ (100). Using the PBE density functional with a Hubbard-U correction to initially probe the potential energy surface of adsorption, we have found a minimum-energy orientation for isopropanol adsorbed on the surface in good agreement with recent sum-frequency generation experiments. Continuing with this minimum, we followed multiple competing pathways and determined necessary transition states and intermediates in order to describe the kinetics and thermodynamics of these reactions. Armed with these results, we elucidate recent experimental findings favoring the formation of the dehydrogenation product acetone over the dehydration product propylene. Finally, we probed the adsorption potential energy surfaces of products in order to describe the contributions of product orientation and lateral surface diffusion to overall reaction dynamics. Our future work will consider different $SrTiO_3$ surfaces such as (111) and (110), as well as different alkanol adsorbates such as ethanol. Overall, these studies provide insight into the fundamental aspects of catalysis of this class of reagents on perovskite surfaces.

Thin Films Division
Room 102A - Session TF+EM+MI+PS-MoA
Thin Films for Advanced Memory Applications and Magnetics

Moderator: Robert Grubbs, Micron Technology

1:40pm **TF+EM+MI+PS-MoA2 ---Multiferroic Integration of Undoped Ferroelectric HfO_2 and Ferrimagnetic $CoFe_2O_4$ Thin films by Radical-Enhanced Atomic Layer Deposition**, *J. Chang,* ***Adrian Acosta,*** *J.P. Chang,* University of California at Los Angeles

Multiferroic materials that exhibit the coexistence and coupling between ferroelectricity and magnetism are of great interest due to their potential for enabling next-generation memories. To overcome the scarcity and weak response of intrinsic multiferroics, composite strategies were proposed to realize robust multiferroic behavior by coupling the properties from constituent ferroelectric and magnetic phases. However, additional challenges for an applicable multiferroic composite are present in the ferroelectric phase since conventional perovskite-based ferroelectrics lack the necessary electrical stability and silicon-compatibility for device integration.

Orthorhombic ferroelectric HfO_2 (FE-HfO_2) based thin films have emerged in the field of microelectronics research owing to its superior compatibility with CMOS technology as well as desirable electrical properties. In this work, multiferroic integration of undoped FE-HfO_2 thin films and ferrimagnetic $CoFe_2O_4$ (CFO) on Si substrates via radical-enhanced atomic layer deposition (RE-ALD) are first demonstrated. For the RE-ALD process, atomic oxygen was utilized in conjunction with TDMAHf and TMHD-based metalorganic precursors for the growth of HfO_2 and CFO respectively. In the composite design, CFO acts as a mechanical constraint to stabilize FE-HfO_2 as well as an active magnetic layer.

Composite ferroelectricity was studied as a function of FE-HfO_2 film thickness as well as post-deposition annealing temperatures. Film crystallinity was investigated through the use of a synchrotron beam source to understand the structural evolution. The induced ferroelectricity was observed to correlate with HfO_2 orthorhombic phase and was maximized when HfO_2 is ~6 nm and after annealing at ~700-800 °C. CFO/FE-HfO_2 composites showed ferroelectric behavior with remnant polarization ~5.5 µC/cm^2 and electrical coercivity ~340-2000 kV/cm, with the potential to be further enhanced via the inclusion of dopants. Comparable magnetism was observed with out-of-plane anisotropy, a saturation magnetization of ~155 emu/cm^3, and a magnetic coercivity ranging from ~1000-3400 Oe. Piezoresponse force microscopy (PFM) verified the strain interaction in the CFO/FE-HfO_2 design. Lastly, a magnetoelectric coupling coefficient of ~5.5×10^{-8} s/m (~55 Oe cm/kV) was obtained from the multiferroic structure with 6-nm thick HfO_2 layer via an *ex situ* poling SQUID magnetometer setup. This work not only highlights the potential of FE-HfO_2 based multiferroic composites in realizing magnetoelectric spintronic devices but also unveils the possibility of utilizing alternative capping layers for achieving multifunctional composite heterostructures.

2:00pm **TF+EM+MI+PS-MoA3 Growth and Characterization of BeO Thin Films Grown by Atomic Layer Deposition using H_2O and O_3 as Oxygen Sources***, **Lee Woo Chul**, C. Cheol Jin,* Center for Electronic Materials, Korea Institute of Science and Technology, Korea*; K. Sangtae,* Center for Electronic Materials, Korea Institute of Science and Technology, Korea*; L. Eric S., Y. Jung Hwan,* Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), South Korea*; H. Cheol Seong,* Department of Materials Science and Engineering, and Inter-University Semiconductor Research Center, College of Engineering, Seoul National University, South Korea*; B. Christopher W.,* Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), South Korea*; K. Seong Keun,* Center for Electronic Materials, Korea Institute of Science and Technology, Korea

BeO has a very large band gap (10.6 eV), which is even larger than that of representative large band gap materials; SiO_2 (~9 eV) and Al_2O_3 (~8 eV). BeO thin films reveal high quality of the interface with Si and semiconductors, showing a possibility as a gate dielectric. Furthermore, rocksalt BeO was recently predicted to have a very high dielectric constant (~ 275) and a very large band gap (10.6 eV). However, the fascinating dielectric properties have not been experimentally realized yet because of the instabilty of the rocksalt BeO. Nowdays, atomic layer deposition (ALD) is a common technique for film growth in a semiconductor industry. The ALD process of the BeO thin films is necessary to be developed to implement BeO in the semicoductor industry. Herein, the growth characteristics and properties of BeO thin films grown by ALD are investigated. We demonstrated that ALD chemistries between dimethylberyllium (DMB) and two different oxygen sources, H_2O and O_3, are governed by different reaction mechanisms, resulting in different film properties.

BeO thin films were grown in a traveling-wave type reactor by ALD with DMB and different oxygen sources, such as H_2O and O_3, in the temperature range of 150 to 300 ^{o}C. Although H_2O-ALD and O_3-ALD of BeO all showed self-saturation behavior, the growth behavior and film properties are strongly dependant on the oxygen sources. With increasing growth temperatures, the growth per cycle (GPC) of H_2O-ALD of BeO decreases, while that of O_3-ALD of BeO is almost constant. The properties of the BeO films grown in H_2O-ALD are nearly temperature-independent, whereas the BeO films grown in O_3-ALD at low temperatures (< 200 ^{o}C) reveal high impurity concentrations and a low film density. These cause lowering of the band gap and dielectric constant of the BeO films grown by O_3-ALD at low temperatures. These findings demonstrate that the O_3-ALD process requires relatively more thermal energy than H_2O-ALD does, to produce high-quality BeO thin films.

2:20pm **TF+EM+MI+PS-MoA4 Atomic Layer Deposition of Magnetic Films and Patterned Features with Tunable Magnetic Properties***, Z. Zhang, **John Ekerdt**,* University of Texas at Austin

We report a process to generate carbon-free Co metal films and patterns by first growing films of CoO via atomic layer deposition on various hydroxylated surfaces and then reducing the CoO at low temperatures to Co metal. The CoO ALD process employs (bis(N-tert butyl, N'ethylpropionamidnato) cobalt (II) and water at 180 °C. Similar processes work for Fe and Ni growth. The metal oxides have a lower density than the metal and will spread uniformly over oxide substrates whereas ultra-thin metal films tend to dewet from the oxide and generate discontinuous films. This dewetting is a strong function of temperature and can be mitigated by lowering the temperature of the reduction process or by lowering the energy of the free surface. Temperatures in excess of 420 °C are required to achieve full reduction of 4.5-nm CoO in H_2 (or D_2); films reduced at this temperature are discontinuous. We report the use of atomic deuterium that is generated over a heated tungsten filament and show that we can fully reduce 4.5-nm CoO to Co at 220 °C without the metal film dewetting oxides such as SiO_2, MgO, ZrO_2, and Al_2O_3. Thermal history of the film is critical to tuning the magnetic properties. As ultra-thin films roughen by extended annealing at 200 °C the film coercivity can be manipulated from 90 to 500 Oe. Since the CoO ALD process is initiated on hydroxylated surfaces and can blocked by organic films, we pattern polystyrene using UV crosslinking through a shadow mask or a diblock co-polymer to generate features ranging from microns to tens of nanometers and deposit CoO on the hydroxylated surfaces that are opened in the polystyrene. This presentation will address the interface issues in achieving selective growth and in manipulating the magnetic properties of continuous Co films and shaped features.

2:40pm **TF+EM+MI+PS-MoA5 Tuning of the Magnetic and Electronic Properties of Epitaxial Heusler Compound Heterostructures***, **Christopher Palmstrøm**,* University of California, Santa Barbara **INVITED**

Heusler compounds have received a lot of attention because of their large range of properties. Their properties depend on the number of valence electrons per formula unit and have been predicted to be semiconductors, metals, ferromagnets, antiferromagnets, half metals, superconductors and topological insulators. Similar to compound semiconductors, the band structure and lattice parameters of Heusler alloys can also be tuned through alloying but over a much larger range of properties. Magnetic tunnel junctions using Heusler alloys that are predicted to be half metals have shown record tunneling magnetoresistance. Heusler half metals have been predicted to have very low Gilbert damping coefficients. They can also be lattice matched to most compound semiconductors and have been used for spin injecting contacts. Recent theoretical predictions suggest that atomic level Heusler superlattices can result in half metallicity and perpendicular magnetization. This presentation will emphasize the molecular beam epitaxial growth combined with in-situ and ex-situ structural, electronic and magnetic characterization of Heusler heterostructures on III-V semiconductors and MgO single crystal substrates. Tuning of their magnetic and electronic properties through elemental substitution to change the number of valence electrons per formula unit and atomic level superlattice growth will be discussed. Examples of Heusler heterostructures and controlling of their magnetic and electronic properties include tuning of the spin polarization in $Co_2Mn_{1-x}Fe_xSi$, Heusler contacts for spin injection into GaAs, spin polarization and magnetic anisotropy of Co_2MnAl/Fe_2MnAl atomic scale superlattices, substitution with Fe in CoTiSb with the aim to convert a semiconductor to half metal and interfacial reactions at Co_2MnSi/MgO interfaces. By careful tuning of the half metallic Heusler film composition, Gilbert damping coefficients <0.001 have been observed.

3:40pm **TF+EM+MI+PS-MoA8 Stabilization of Ferroelectric Phase of $Hf_{0.5}Zr_{0.5}O_2$on NbN at 4 K***, **Michael David Henry**, S. Smith, R. Lewis,* Sandia National Laboratories*; J. Ihlefeld,* University of Virginia

This work demonstrates cryogenic ferroelectric behavior of atomic layer deposited (ALD) hafnium zirconium oxide (HZO) using reactively sputtered niobium nitride electrodes. With the discovery of ferroelectricity in doped HfO_2, perturbations of the dopants expanded from silicon into mixtures utilizing yttrium and zirconium and with electrodes ranging from platinum to nitrides such as titanium nitride and tantalum nitride. This set of materials have demonstrated stabilizing a crystalline phase permitting both ferroelectric and anti-ferroelectric behaviors to have been observed. With the atomic similarities between Ta and Nb, a natural extension the electrode materials' set to include NbN was explored in this work.

Devices tested at both room temperature (RT) and under cryogenic conditions demonstrated ferroelectric behavior as determined by polarization vs. electric field (P-E) loops. The polarization results show comparable ferroelectric behavior at room temperature and 4 K, however the effect of the dielectric polarization is combined with the remnant polarization (P_r) in this measurement. To separate the two effects, remnant polarization sweeps were performed and plotted only displaying the P_r. A typical measurement on a 170 mm diameter device, was performed starting at 4 K and ending at 150 K. By adding the positive and negative $P_r$with the electric field at 0 MV/cm ($2P_r$), polarization was observed to decrease as the stage was warmed up. A second known behavior of ferroelectrics is the so-called wake-up effect where the ferroelectric phase is understood to be stabilized by oxygen movement as a positive and negative voltage is applied. Here, a 3 V square wave at 1Hz was utilized in 60 second intervals with $P_r$loops performed before and after each wake-up cycling at room temperature. The $2P_r$was seen to come to steady state after approximately 100 seconds. Remnant polarization at the conclusion of 360 seconds is seen to have polarization approximately 10 mC/cm^2, a value comparable to other findings. Polarization values of approximately 10 mC/cm^2suggest that these ferroelectric films could be utilized with superconductors at liquid He temperatures for a new class of superconductor-ferroelectric based devices.

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4:00pm **TF+EM+MI+PS-MoA9 Atomic Layer Deposition of Co/Pt Multilayer films for Perpendicular Magnetic Anisotropy***, **Devika Choudhury**, A.U. Mane, C.M. Phatak, A.K. Petford Long, J.W. Elam,* Argonne National Laboratory

"Smaller, Faster and Efficient" are the key words describing the ever increasing need of data-storage industry.[1] This demand has brought about a shift from longitudinal recording in magnetic media to perpendicular recording, where magnetic bits are perpendicular to the plane of the recording media instead of being in the same plane. Significantly higher storage density is obtained as a result of using the perpendicular magnetic recordings utilizing materials demonstrating perpendicular magnetic anisotropy (PMA). Strong PMA is usually observed in ultrathin films of ferromagnetic metals like Co and Fe forming alloys with heavy metals like Pt, Pd, Au and Ta.[2] Of them Co/Pt alloys and multilayer structures are probably the most widely investigated system for understanding the PMA origin and behavior.

The effective anisotropy energy of the multilayer films in the PMA regime depends on various factors like thickness of the individual Co/Pt layers, quality of interfaces and crystallinity of the films.[3] Till date, the commonly used techniques for growth of Co/Pt multilayers have been electron beam evaporation and sputtering. However, for development of higher areal density using three-dimensional media, conformal, uniform and controlled deposition of the thin films is certainly required.

In this work, we utilize atomic layer deposition (ALD) of Co/Pt multilayers to overcome limitations of the other growth processes. ALD provides precise control over the film thickness along with uniform and conformal films thus resulting in distinct sharp interfaces between the individual metal films. Bis(N-t-butyl-N'-ethylpropanimidamidato)cobalt(II) and hydrogen precursors are used for Co ALD while Trimethyl(methylcyclopentadienyl)platinum(IV) and water are used as precursors for Pt deposition. QCM studies confirm self-limiting ALD growth nature of the individual metal films at 300°C. Pt(10nm)/[(Co/Pt)x8](16nm)/Pt(2nm) stacks are grown using alternate cycles of Co and Pt. QCM measurements reveal a short nucleation regime of Pt over Co films. HRTEM imaging and XPS analysis of the multilayer stacks are utilized to study the interfaces of the multilayer films closely. Preliminary SQUID measurements show a change in anisotropy between pure Co and Co/Pt multilayer films. Effects of variation in individual layer thicknesses, deposition temperature, post-deposition annealing temperature etc. remains to be seen.

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Thin Films Division

Room 104B - Session TF-MoA

IoT Session: Thin Films for Photovoltaics

Moderators: Matthew Richard Linford, Brigham Young University, Joe Becker, Kurt J. Lesker Company

1:20pm **TF-MoA1 Atomic Layer Deposition for Organic and Perovskite Solar Cells***, **Thomas Riedl**,* University of Wuppertal, Germany **INVITED**

Organic and perovskite based solar cells (OSCs / PSCs) provide an intriguing avenue for next-generation thin-film photovoltaics. Aside from the photo-active material, the choice of charge extraction layers (CELs) substantially impacts performance and lifetime. For OSCs, the use of ALD-grown tin-oxide (SnO_x) as electron extraction layer (EEL) mitigates two critical issues, i.e. light soaking[1] and photo-shunting[2], which frequently occur in case ZnO based EELs are used. In tandem OSCs, all-oxide recombination interconnects based on high work-function (WF) MoO_x and low-WF ALD grown SnO_x show ideal alignment of the conduction band of MoO_x and SnO_x and loss-free addition of the open circuit voltages of the two sub-cells.[3]

In the second part, I will show ALD-grown SnO_x as impermeable EEL for PSCs to enable impressive stability of the cell against heat and moisture. The SnO_x is positioned between the metal electrode and the perovskite. Its outstanding permeation barrier properties[4] protect the $MAPbI_3$ against the ingress of moisture or migrating metal atoms, while simultaneously the metal electrode is protected against leaking halide compounds. Thereby, PSCs with an efficiency of >20% and outstanding long-term stability can be achieved. They remain stable over 4500 hours at elevated temperatures as well as in ambient air. [5,6] ALD-grown SnO_x is also excellently suited to sandwich and protect ultra-thin metal layers (Ag or Cu) as cost efficient Indium-free semitransparent electrodes (SnO_x/metal/SnO_x) in PSCs. Using photoelectron spectroscopy, we unravel the formation of a PbI_2 interfacial layer between a SnO_x EEL and the perovskite. The resulting interface dipole between SnO_x and the PbI_2 depends on the choice of oxidant for ALD (water, ozone, oxygen plasma). SnO_x grown by using ozone affords hysteresis-free devices with a stable efficiency of 16.3% and a very high open circuit voltage of 1.17 V.[7] Ultimately, SnO_x grown by spatial-ALD at atmospheric pressure is presented. Its suitability to replace its low pressure analogues in PSCs is shown. [1, 2] This work paves the way towards roll-to-roll fabrication of stable, Indium-free PSCs.

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2:00pm **TF-MoA3 Insights into ALD Al_2O_3 Growth on Hybrid Organic-Inorganic Perovskite***, **Dibyashree Koushik**[1], L. Hazendonk,* Eindhoven University of Technology, The Netherlands*; V. Zardetto,* TNO-Solliance, The Netherlands*; W.M.M. Kessels, M.C. Creatore,* Eindhoven University of Technology, The Netherlands

The need for environmentally stable perovskite solar cells (PSCs) has promoted the quest for moisture and thermal stress barrier layers that can adequately seal the perovskite absorber. Atomic layer deposited (ALD) metal oxides are widely acknowledged for their continuous and pinhole-free nature, derived from the self-limiting deposition process. We have recently shown that 10 cycles of ALD Al_2O_3 deposited directly on top of $CH_3NH_3PbI_{3-x}Cl_x$ perovskite are effective in delivering a superior PSC performance with 18% efficiency (compared to 15% of the Al_2O_3-free cell) and long-term humidity-stability of more than 60 days.[1,2] Motivated by

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[1] **TFD James Harper Award Finalist**

these results, the present contribution focuses on the chemical modifications which the $CH_3NH_3PbI_{3-x}Cl_x$ perovskite undergoes upon growth of ALD Al_2O_3. Specifically, we couple *in situ* infrared spectroscopy studies during film growth, with XPS analysis of the ALD Al_2O_3/perovskite interface. The IR-active signature of NH_3^+ stretch mode (asymmetric at 3179 and symmetric at 3132 cm^{-1}) of the perovskite undergoes minimal changes upon exposure to ALD cycles, indicating no diffusion of the ALD precursors (TMA and H_2O) into the bulk of the perovskite. The exclusion of H_2O infiltration is evident also from the absence of two well-defined peaks at 3500 and 3450 cm^{-1}. These conclusions are supported by Doppler broadening-positron annihilation spectroscopy studies, revealing no changes in the open volume of 'bulk' perovskite upon deposition of Al_2O_3. Analysing the differential IR spectra (Absorbance$_{\text{(perovskite + Al2O3)}}$-Absorbance$_{\text{(pristine perovskite)}}$) with increasing ALD cycles, the abstraction of NH_3^+ from the perovskite surface is discerned, with the appearance of negative N-H stretch and bend modes. In parallel, the growth of ALD Al_2O_3 on perovskite is witnessed by the characteristic IR-active Al-O-Al phonon and (OH)-Al=O stretch modes. Based on the XPS analysis, a plausible growth mechanism of ALD Al_2O_3 on top of perovskite is discussed. During the first half- cycle, TMA reacts with perovskite via the interaction of one of its methyl groups with one of the H atoms of $CH_3NH_3^+$ of perovskite. This interaction weakens the hydrogen-bonds between $CH_3NH_3^+$ and I^- of the perovskite, resulting in breakdown of the organic moiety from the inorganic framework. CH_3NH_2 and CH_4 are released as byproducts, leaving behind an adduct comprising of PbI_3-$Al(CH_3)_2$. In the next half-cycle of H_2O dosage, the H_2O molecule can react with the PbI_3-$Al(CH_3)_2$ adduct and generate the –OH surface sites necessary to promote the growth of Al_2O_3.

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2. D. Koushik *et al.*, *Adv. Mater. Inter.*, **2017**, *4,* 1700043.

2:20pm **TF-MoA4 Single Junction GaAs Thin Film Solar Cells on Flexible Metal Tapes for Low Cost Photovoltaics***,* ***Devendra Khatiwada***[1]*, M. Rathi, P. Dutta, S. Sun, Y. Yao, Y. Gao, Y. Li, S. Pouladi, J.-H. Ryou, V. Selvamanickam,* University of Houston

III-V semiconductor materials like GaAs that have a high absorption coefficient in the relevant energy range for photovoltaic absorbs most of the sunlight within small range beneath the surface. Highest efficiencies have been reported in III-V solar cells based on GaAs wafer. However, its application has been very limited due to high cost of these wafers. We develop a technology to provide high quality epitaxial semiconductor thin films on low-cost flexible metal tapes by roll to roll fabrication to overcome the wafer cost .

Herein, we introduce high quality epitaxial semiconductor thin film on low cost flexible metal (Hastelloy) to provide flexibility and overcome the wafer cost with roll to roll processing. Firstly, polycrystalline to single crystalline like material were grown on the flexible metal tape over which biaxially textured Germanium (Ge) thin film were grown. Finally, epitaxial (Al) GaAS semiconductor thin films were grown on the biaxially textured Ge thin films using Metal Organic Chemical Vapor Deposition (MOCVD). The device were further processed for contact deposition via photolithography process.

The fabricated thin film III-V solar cells showed promising photovoltaic efficiency under A.M 1.5G with front illumination geometry. Photon conversion efficiency greater than 11% was observed under A.M 1.5 (1 sun) with open circuit voltage (V_{OC}) of 642mV, short circuit current density (J_{SC}) of 25mA/cm^2 and fill factor (FF) of 70% . Further improvement in device efficiency is achieved with new device architectures, optimization of the growth and improving fabrication processes.

This work was partially funded by the U.S. Department of Energy Sunshot Initiative.

2:40pm **TF-MoA5 New Insights into the Microstructure and Composition of New Generation CdSeTe/CdTe/MZO Photovoltaic Devices***, T.A.M. Fiducia, A. Abbas,* Loughborough University, UK*; K. Li, C.R.M. Grovenor,* University of Oxford, UK*; A. Munshi, K.L. Barth, W.S. Sampath,* Colorado State University*;* ***John Walls,*** Loughborough University, UK

Thin film polycrystalline Cadmium Telluride solar cells are the lowest cost solar technology. Recent improvements in the device architecture have increased device conversion efficiency and lowered costs still further. The traditional semi-absorbing cadmium sulphide window layer has been replaced with higher band gap alternatives such as magnesium-doped zinc-oxide (MZO). Also Selenium has been added to the near-junction interface region in the CdTe absorber layer which becomes graded during the cadmium chloride activation process and increases carrier lifetime. In this paper we report on microstructural and composition studies using STEM and EDX on device cross-sections along with the use of Nano-SIMS to provide 3-Dimensional chemical maps of the cells at high resolution and sensitivity. These microstructural analyses are correlated with electrical measurements from the devices. The analysis of chlorine and selenium in these cells reveals the different types of diffusion modes involved in 3 dimensions. It provides new insights into the passivation mechanisms at work in grain boundaries. It also provides the first direct evidence for passivation of incoherent twin facets and incorporation of chlorine and selenium in grain interiors. Improved understanding of the ways these new devices work will determine how they may be improved still further.

3:00pm **TF-MoA6 Schottky Barrier Metal-Insulator-Silicon Photovoltaics: Influence of Fixed Charge and Dipoles in Atomic Layer Deposited Alumina***,* ***Nicholas Strandwitz,*** Lehigh University

Metal-insulator-semiconductor Schottky barriers are a potentially low-cost photovoltaic configuration. The PV figures of merit are strongly influenced by the interface composition and structure. Our group has used atomic layer deposition (ALD) to create well-defined alumina-based insulators in which the thickness, fixed charge, and composition can be well-controlled. Based on a simple electrostatic model, fixed charge in the insulator can be used to modify barrier heights, and the fixed charge at ALD alumina-silicon interfaces can be tuned over a range of approximately 5E12 cm^{-2}, making this system an ideal test-bed to understand the role of fixed charge experimentally. We find little to no influence of the fixed charge characteristic of the alumina-silicon interface in our experiments, and that barrier heights appear to be dominated by interface dipoles. We relate our results to previous experimental and theoretical work that relates dipole strength to differences in oxygen areal densities at the silicon oxide-aluminum oxide interface. We also report preliminary PV figures of merit for our well-controlled MIS junctions.

3:40pm **TF-MoA8 Sulfur Vacancies as the Origin of *n*-type Doping in Pyrite FeS_2Single Crystals***, B. Voigt, W. Moore, J. Walter, D. Ray, M. Manno,* University of Minnesota*; J.D. Jeremiason,* Gustavus Adolphus College*; L. Gagliardi,* ***Eray Aydil****, C. Leighton,* University of Minnesota

Pyrite FeS_2 is an ideal photovoltaic material for low-cost and sustainable thin film solar cells because it is composed of earth-abundant, non-toxic, inexpensive elements, has a suitable band gap well-matched to the solar spectrum, and absorbs light so strongly that a 100 nm thick film is adequate to absorb over 90% of all photons with energies above the band gap. While pyrite FeS_2 was pursued vigorously in the 1980's as a potential solar cell material, efficiencies never exceeded 3 %. One of the fundamental problems was a lack of control over doping. Recently, rigorously phase-pure pyrite FeS_2 single crystals and thin films were shown to be exclusively *n*-type, with a universal dependence of electron mobilities in both thin films and crystals on Hall coefficient suggesting that a common dopant is responsible for this *n*-type behavior. This dopant, however, has not been identified. We have amassed the strongest evidence to date that sulfur vacancies are this common dopant. Single crystals with experimentally indistinguishable lattice parameters, mosaic spread, and nominal stoichiometry, grown via chemical vapor transport under different sulfur vapor pressures, show significantly different electron densities and mobilities. Specifically, crystals grown under high sulfur vapor pressure exhibit semiconducting behavior and temperature-dependent electron densities with an activation energy of 225 meV. Decreasing the sulfur vapor pressure during crystal growth decreases this activation energy, increases the electron density and mobility, and triggers metal-like conduction observed in temperature-dependent resistivity measurements. This is consistent with higher concentrations of sulfur vacancies in pyrite crystals grown under decreased sulfur vapor pressure. These trends are independent of transition metal impurity concentrations and, importantly, electron densities are too large to be explained by trace amounts of transition metal impurities. All evidence thus implicates sulfur vacancies as the ubiquitous *n*-type dopant in pyrite FeS_2.

Work supported by the Xcel Energy Renewables Development Fund and the University of Minnesota NSF MRSEC under DMR-1420013.

4:00pm **TF-MoA9 Strong Effect of Reaction Temperature on the Nucleation of Atomic Layer Deposition of Al_2O_3 on Methylamine Lead Perovskite***,* ***Xiaozhou Yu****, H.M. Yan, Q. Peng,* University of Alabama

Hybrid perovskite solar cells have attracted tremendous attention due to the low cost and high-power conversion efficiency. The biggest barrier to its commercialization is the poor stability in the outdoor environment.Al_2O_3 atomic layer deposition (ALD) has shown great promise in improving the

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[1] **TFD James Harper Award Finalist**

environmental stability of hybrid perovskites, however, the nucleation of ALD Al_2O_3 on perovskite has not yet been understood, especially the reaction between tri-methyl aluminum (TMA), a strong Lewis acid, and fresh hybrid perovskites. In our work, the growing behavior and surface reaction mechanism of Al_2O_3 ALD (Trimethyl Aluminum (TMA) and H_2O chemistry) on $CH_3NH_3PbI_3$ perovskite is studied systematically by *in situ*quartz crystal microbalance(QCM) and *in situ*quadrupole mass spectrometers (QMS).We find that the reaction temperature is the key parameter affecting the nucleation of Al_2O_3 ALD on $CH_3NH_3PbI_3$. At 25°C, TMA can accumulate mass onto the surface of a fresh $CH_3NH_3PbI_3$ substrate through substrate site-limited reactions. The surface passivation provided by TMA adsorption at 25°C improves the ambient stability of $CH_3NH_3PbI_3$. In contrast, at 75°C, TMA etches $CH_3NH_3PbI_3$ by the formation of volatile products, which will degrade $CH_3NH_3PbI_3$ to PbI_2.

4:20pm **TF-MoA10 Synthesis of Gas Barrier Coatings for Hybrid Halide Perovskites by Atomic Layer Deposition***, X.Z. Yu, H.M. Yan,* ***Qing Peng****,* University of Alabama

Atomic layer deposition of oxide film on shows a great promise to dramatically improve the ambient stability of hybrid halide perovskite. The nucleation of an ALD oxide on PCBM ([6,6]-phenyl-C61 butyric acid methyl ester) is critical to reliably apply this strategy. In this paper, we present the first study of the nucleation behaivor of ALD oxides, including Al_2O_3 and ZnO on PCBM. We find PCBM film acts a gas diffusion barrier blocking the ALD reactants (diethyl zinc) from etching the underlying $CH_3NH_3PbI_3$. However, ZnO is not able to nucleate on PCBM. We further identify that trimethyl aluminum, a strongly Lewis acid, reacts readily with C=O on PCBM to generate a seeding layer for nucleating ZnO ALD. This new chemical route is highly reliable and can be used to synthesize ALD ZnO coatings over PCBM. The synthesized PCBM/Al_2O_3-ZnO dramatically improves the stability of $CH_3NH_3PbI_3$ against the ambient and even against liquid water. The result signifies the importance of understanding of nulceation of ALD in enabling reliable barrier coatings for hybrid halide perovskite.

Vacuum Technology Division
Room 203B - Session VT-MoA

Pumping and Outgassing

Moderators: James Fedchak, NIST, Giulia Lanza, SLAC National Accelerator Laboratory

1:20pm **VT-MoA1 Gas Adsorption and Desorption Properties of 3D Printed Objects***,* ***Matt Hartings,*** American University*; J. Scherschligt, J.A. Fedchak, Z. Ahmed,* National Institute of Standards and Technology **INVITED**

Additive manufacturing processes are enabling technologies, supporting advances in a number of applications where either controlled gas uptake and release or the maintenance of a good vacuum environment are critical. In each of these scenarios, a detailed understanding of how a 3D printed object interacts with gas molecules is necessary to advancing how these objects can be used in a technical setting. I will describe two 3D printed systems and their outgassing properties. In the first system, we have compared traditionally machined vacuum chambers, made of either steel or titanium, with their 3D printed counterparts. We have evaluated hydrogen outgassing at low pressures for each of these systems and analyze how the surface micro- and nano-scale structure affects these measurements. In doing so, we assess how different printing parameters can affect outgassing of the object of interest. In the second system, we have studied the gas uptake, retention, and controlled gas adsorption of polymer composites that contain metal organic framework (MOF) particles. MOFs are a relatively new class of materials that have been implicated in a number of gas storage and delivery applications. We have 3D printed objects with our polymer-MOF composite materials and have evaluated the dynamics with which they adsorb and desorb hydrogen and nitrogen. We have found that chemical interactions between the MOF and the polymer can help to support or diminish the capacity to effectively store gas. Our work in both of these areas has shown how additive manufacturing processes can help to further technological goals while delineating the work that remains to successfully incorporate 3D printing objects into commercial devices.

2:00pm **VT-MoA3 Outgassing, Desorption, and Gas Uptake of 3D-Printed Materials***,* ***James Fedchak,*** NIST*; J. Scherschligt, Z. Ahmed,* National Institute of Standards and Technology*; M. Hartings,* American University

We are investigating the outgassing, gas uptake, and gas desorption properties of novel 3D-printed composite materials, 3D-printed metals, and heat-treated metals. Materials we have investigated include 3D-printed titanium, stainless-steel, and composites of acrylonitrile butadiene styrene (ABS) melt-blended with metal-organic framework (MOF) materials. We have performed measurements of the outgassing into vacuum, the gas absorption of atmospheric gases such as H_2, N_2 and water at pressures greater than 50 kPa, and the desorption of the gases into vacuum. There are three motivations behind these investigations: first, we are interested in producing ultra-high vacuum (UHV) and extreme-high vacuum (XHV) pressures in small devices for quantum sensor and quantum science applications, such as our cold-atom vacuum sensor (CAVS). Second, we are interested in using novel new materials for gas sensing and, third, we are interested in using these composite materials for gas storage and separation. We will present our most interesting and recent results from these studies. For example, the ability of MOFs to store gas is now well-known, but our studies show that the MOFs retain their gas-absorption properties within the 3D-printed MOF-ABS composites.

2:20pm **VT-MoA4 Performance Prediction Approaches for Liquid Ring Vacuum Pumps with Mercury as Working Fluid***,* ***Santiago Ochoa Guaman,*** *T. Giegerich,* Karlsruhe Institute of Technology, Germany*; C. Dahlke,* HERMETIC-Pumpen GmbH, Germany*; C. Day,* Karlsruhe Institut of Technology (KIT), Germany

In the European fusion reactor (DEMO) development program, continuous working vacuum pumps are foreseen to pump the reactor. The pumps have to process large amounts of tritium, a radioactive and chemically very active gas. In a systems engineering approach, a pumping solution based on liquid ring pumps (LRPs) and diffusion pumps has been identified. Mercury is the only fluid perfectly tritium compatible and will be applied as working fluid.

LRPs exist for around 130 years and several mathematical approaches have been developed for its 1D modelling. Diagrams and tables also have been produce from experiments for fluid densities between 800 kg/m^3 to 1200 kg/m^3 but mostly for water as working fluid and with air as pumped gas. Modern 3D simulation tools have not been applied so far for analyzing these pumps. Thus, in order to design and analyze the operating behavior of LRPs with mercury as working fluid, it is necessary to design a special code for the prediction of the thermodynamic and operational behavior of LRPs operating with high density working fluids.

This great challenge is presented in this work, starting with the development of a simulation code based on three already existing methods. For its benchmarking against literature data, water as working fluid and air as pumped gas will be used. In a follow-up step, the code will be run considering mercury as working fluid. These results will be discussed against experimental results produced at the THESEUS vacuum pump test facility at KIT.

In the second part of this work, a two-phase three-dimensional CFD model will be performed using a more detailed pump geometry. Goal of this activity is to achieve a more accurate description of the pump performance without the use of empirical parameters. This requires extensive modelling and high computational effort. The status of this task will be presented in this paper and first results will be shown and benchmarked against experiments and the code.

2:40pm **VT-MoA5 Particle Emission from Ion Pumps: Optimized Shielding without Severe Conductance Limitation***,* ***Mauro Audi****, C. Paolini,* Agilent Technologies, Italy*; P. Manassero,* Agilent Technologies

Charged particle emission from ion pumps is a potential major concern in sensitive applications such as Electron Microscopes , Particle Accelerators and Synchrotron Light Sources .

In fact , emitted positive ions and electrons can affect the performance of the machine or the resolution of the instrument.

Optical shield can be used to limit the number of emitted particles , but standard existing solutions have major conductance limitations as an unwanted side effect .

A test campaign on various shielding designs was carried out with a Faraday Cup powered at different bias voltage at the inlet of the ion pump , and the tests were repeated at different operating pressures and voltages .

Test results demonstrate that it is possible to reduce the number of charged particles by three orders of magnitude with minor conductance limitation and consequently maintaining a high fraction of the original ion pump pumping speed .

3:40pm **VT-MoA8 VTD Early Career Award Invited Talk: The Development of the Spacecraft Atmosphere Monitor*, Steven Schowalter*[1]*,*** Jet Propulsion Laboratory **INVITED**

In this talk I will focus on our team's recent development of the Spacecraft Atmosphere Monitor (SAM), a miniaturized Gas Chromatograph Mass Spectrometer slated to be commissioned as a Technology Demonstration Unit on the International Space Station in early 2019. The sensor system for this instrument consists of a quadrupole ion trap mass spectrometer coupled with a MEMS preconcentrator, gas chromatograph, and valve system. The SAM has been designed to monitor major constituents as well as trace organic contaminants in the atmospheres of crewed spacecraft. The requirements of spaceflight have placed stringent constraints on the instrument design which have led to a highly-intentionally designed vacuum system. The vacuum chamber is manufactured by a custom additive process and is equipped with novel differential pumping and gas inlet architecture. The design of this vacuum system will be detailed and preliminary data will be presented.

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[1] **VTD Early Career Award**

2D Materials Focus Topic
Room 201B - Session 2D+EM+MI+NS-TuM

Properties of 2D Materials including Electronic, Magnetic, Mechanical, Optical, and Thermal Properties

Moderator: Johannes Jobst, Leiden University

8:00am **2D+EM+MI+NS-TuM1 Effect of Lattice Stacking Orientation and Local Thickness Variation on the Mechanical Behavior of Few Layer Graphene Oxide***, **Teng Cui**, S. Mukherjee, C.H. Cao, P.M. Sudeep, J. Tam,* University of Toronto, Canada*; P.M. Ajayan,* Rice University*; C.V. Singh, Y. Sun, T. Filleter,* University of Toronto, Canada

Investigation of few layer 2D materials is fundamentally important to bridge the gap between monolayer and bulk properties, and practically meaningful for applications as reinforcement nanofillers and layered electronic devices. Few layer introduces differences from intrinsic properties of monolayers due to the complexity of structural heterogeneities, such as lattice stacking orientation and local thickness variation. In this work [1], few layer graphene oxide (GO) with different structural heterogeneities were studied using atomic force microscopy-based deflection measurements and transmission electron microscopy (TEM). Direct TEM evidence of fracture surfaces and molecular dynamics (MD) simulations revealed decoupled and dissimilar layer crack patterns (i.e., different cracking pathway of top and bottom layers) for misaligned bilayer GO. In contrast, aligned GO bilayers generally fractured with a larger portion of common cracks shared by both layers, indicating stronger interlayer interaction than its misaligned counterpart. MD results also revealed insignificant effect of lattice alignment on the strength and toughness of GO bilayers, which is ~23.5 GPa and $\sim 1.71\times10^{-18}$ J/nm^3, respectively, for both aligned and misaligned cases. Scaling up to ~5 layers and above revealed more significant local thickness heterogeneity and consequently a ~60% reduction of the normalized fracture force and toughness with respect to the average number of layers. MD simulations on partially intercalated few layer GO revealed anisotropic and heterogeneous stress distributions, as well as stress concentration near the inner edges, which may account for the significant reduction of strength and toughness.

[1] T. Cui, S. Mukherjee, C. Cao, P. M. Sudeep, J. Tam, P. M. Ajayan, C. V. Singh, Y. Sun, and T. Filleter, "*Effect of Lattice Stacking Orientation and Local Thickness Variation on the Mechanical Behavior of Few Layer Graphene Oxide*", **Carbon**, accepted.

8:20am **2D+EM+MI+NS-TuM2 Out-of-Plane Mechanical Properties of 2D Hybrid Organic-Inorganic Perovskites by Nanoindentation***, **Qing Tu**, I. Spanopoulos, S. Hao, C. Wolverton, M. Kanatzidis, G. Shekhawat, V. Dravid,* Northwestern University

2D layered hybrid organic-inorganic perovskites (HOIPs) have demonstrated improved stability and promising photovoltaic performance. The mechanical properties of such functional materials are both fundamentally and practically important to achieve both high performance and mechanically stable (flexible) devices. Here we report the static, out-of-plane mechanical properties of a series of 2D layered lead iodide HOIPs with a general formula of $(R\text{-}NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$, and investigate the role of structural sub-units (*e.g.*, the length of theorganic spacer molecules -R and the number of inorganic layer -n) on the mechanical properties by nanoindentation. We find that the 2D HOIPs are softer than their 3D counterparts due to the replacement of the strong inorganic layer and ionic bonds by the soft organic layers and the weak Van der Waals interactions. As n increases from 1 to 5, the relative amount of these weak factors in the crystals are decreasing and both the out-of-plane Young's modulus E and hardness H increase, approaching to the reported values of corresponding 3D crystals. DFT simulations showed a similar trend to the experimental results. Furthermore, we show that increasing the alkyl chain spacer molecule -R from $-C_4H_9$ to $-C_{12}H_{25}$, E first decreases and eventually plateaus while no clear trend in H is observed. Our results reveal that the competition between the stiff inorganic layers, the soft organic layer and the weak Van der Waals interfaces determines the mechanical properties of 2D HOIPs. Finally, we compare these findings with those in other 2D layered materials such as h-BN, MoS_2 and MXene, and shed light on routes to further tune the out-of-plane mechanical properties of 2D layered HOIPs.

8:40am **2D+EM+MI+NS-TuM3 Mechanical Properties of Many-layer CVD Graphene***, **Kyle Larsen**, S. Lehnardt, J.T. Rowley, B. Anderson, R.R. Vanfleet, R.C. Davis,* Brigham Young University

Graphene, a monoatomic layer of carbon atoms, has a reported Young's modulus of 1 TPa and a tensile strength of 130 GPa. These values make it both the strongest and one of the stiffest materials ever reported. The mechanical properties of multilayer graphene grown by chemical vapor deposition have been reported for films of up to 10 layers (3.35 nm). Films thicker than about 10 layers (sometimes considered graphite rather than multilayer graphene) are of interest as membranes and in MEMS applications. We have characterized CVD grown many-layer graphene films with thicknesses of about 50 nm by Raman spectroscopy, burst testing, and atomic force microscopy. The atomic force microscope was used to map the local compliance over suspended regions containing cantilevers cut out of the many-layer graphene with a focused ion beam. Analytical and finite element modeling were used in the analysis of the deflection of the many-layer graphene cantilevers to extract Young's modulus. The many-layer graphene is high quality (little or no D peak in the Raman spectrum) and has a Young's modulus in the range reported for graphene (0.5 TPa to 1 TPa).

9:20am **2D+EM+MI+NS-TuM5 Discovering and Visualizing Ferromagnetism in Intrinsic Two Dimensional Materials***, **Jing Xia**,* University of California Irvine **INVITED**

In this talk, I will discuss our recent results on discovering and visualizing in 2D magnetism using a unique scanning Sagnac MOKE microscope, which is based on a Sagnac interferometer technique and has achieved unprecedented nano-radian level Kerr and Faraday sensitivity even at DC. In exfoliated Cr2Ge2Te6 (CGT) atomic layers, we report the discovery of intrinsic ferromagnetism in 2D van der Walls crystals, defying the well-known Mermin-Wagner theorem. Unlike 3D magnetism, the ferromagnetic order in this 2D system is stabilized by magnetic anisotropy from the CGT structure, which is not present in graphene. As a result, changing the magnetic anisotropy with a small external magnetic field was found to strongly enhance the Curie temperature, which is a feature unique to 2D magnetism.

11:00am **2D+EM+MI+NS-TuM10 Onset of Buckling Folding and Slipping Instabilities in 2D Materials under Compressive Strain***, **Jaehyung Yu**, E. Ertekin, A.M. van der Zande,* University of Illinois at Urbana-Champaign

Atomic membranes of monolayer 2D materials represent the ultimate limit in size of nanoelectromechanical systems. These materials have high mechanical strength, yet low bending modulus leading to high pliability. Adding in the diverse active electronic properties of different 2D materials, atomic membranes will allow new next generation technologies like highly strainable crumpled or folded electronics, or 3D origami devices based on 2D materials. In order to realize these new technologies it is important to understand how the rules of continuum membrane mechanics break down on the atomic scale and how these deformations will affect the electronic properties, including the role of compressive stress, bending, adhesion and interlayer shear.

Here, we present a combined experimental and theoretical study of the onset of instabilities such as buckling, folding and slip on the properties of 2D materials and heterostructures under compression. We generate periodic fold structures of the graphene, MoS2, and their heterostructures by introducing the compressive stresses with the pre-strained stretchable substrate. We analyzed then measured the membrane morphology using atomic force microscopy (AFM) under increasing levels of uniaxial compression up to 30%. We observed that the strain-relaxation mechanism of atomic membranes could be varied from generating and growing standing folds to collapsing to generate trifolds based on the mechanical properties including 2D modulus, bending stiffness, adhesion and interlayer shear energies. The onset of these instabilities depends on the 2D material or heterostructure making up the membranes. In graphene folds grow then collapse at compressive strain of ~5%. In monolayer MoS2 standing folds grow to a fixed height of ~20 nm but do not collapse. Instead, new folds are generated in between the existing folds.

We use density functional theory (DFT) to model the morphology of the same structures under compressive slack. We find that, in multi-layer 2D materials, the onset of slip between the layers is crucial parameters to decide the bending stiffness of the material. We found that the superlubricity between the layers allows the linear scaling of bending stiffness with the number of layers, which violates the conventional cubic scaling of bending stiffness in continuum mechanics.

We unite the atomic scale simulation with the experiment through a continuum model to compare the period, shape, and transition strains extract the variations in adhesion and bending energy of different 2D materials and heterostructures to find the deformation of 2D materials under the compressive strain.

11:20am **2D+EM+MI+NS-TuM11 Title: Spatially-Resolved Contact-Free Electrical Characterization of Transition Metal Dichalcogenide Films Grown by Chemical Vapor Deposition.***, **Miguel Isarraraz**, L. Bartels,* University of California, Riverside

Surface Acoustical Waves (SAWs) and Transition Metal Dichalcogenides (TMDs), separately, are topics of current research due to their present and future use in telecommunications and beyond-CMOS technology. The interaction between a SAW and a 2D electron gas has been previously studied by measuring the absorption of the SAW by GaAs and, more recently, graphene[i,ii,ii]. Here, the interaction between a SAW and a TMD is studied using MoS_2 directly grown by chemical vapor deposition on 128°YX-cut $LiNbO_3$. By focusing a 532 nm laser on the sample, the generation of electron-hole pairs is found to enhance the attenuation of the SAW as expected, and this technique can be used to spatially resolve variations inside triangular MoS_2 islands. Furthermore, the time dependence of the SAW attenuation with laser exposure is used to distinguish between heating and electronic effects. The induced acoustoelectric current, laser power, and SAW excitation power dependence are discussed. This technique provides a means of electrically characterizing atomically thin semiconducting film that avoids the limitations of metallic contacts.

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[iii] Miseikis, V.; Cunningham, J. E.; Saeed, K.; O'Rorke, R.; and Davies, A. G., Acoustically induced current flow in graphene. Appl. Phys. Lett. **100**, 133105 (2012); https://doi.org/10.1063/1.3697403

11:40am **2D+EM+MI+NS-TuM12 Electronic, Thermal, and Unconventional Applications of 2D Materials***, **Eric Pop**, E. Yalon, C. McClellan, K. Smithe, C. English, M. Mleczko, M. Muñoz Rojo, N. Wang, S. Suryavanshi, I. Datye, C. Bailey, A. Gabourie, M. Chen, V. Chen, K. Schauble, R. Grady,* Stanford University **INVITED**

This talk will present recent highlights from our research on two-dimensional (2D) materials and devices including graphene, boron nitride (h-BN), and transition metal dichalcogenides (TMDs). The results span from fundamental measurements and simulations, to devices, to system-oriented applications which take advantage of unusual 2D material properties. On the fundamental side, we have measured record velocity saturation in graphene [1,2], as well as the thermal properties of graphene nanoribbons [3]. These are important for electronic applications, which can exhibit substantial self-heating during operation [4]. Taking advantage of low *cross-plane* thermal conductance, we found unexpected applications of graphene as ultra-thin electrode to reduce power consumption in phase-change memory [5]. We have also demonstrated wafer-scale graphene systems for analog dot product computation [6].

We have grown monolayer 2D semiconductors by chemical vapor deposition over cm^2 scales, including MoS_2 with low device variability [7], WSe_2, $MoSe_2$ – and multilayer TMDs $MoTe_2$ and WTe_2 [8]. Importantly, $ZrSe_2$ and $HfSe_2$ have native high-K dielectrics ZrO_2 and HfO_2, which are of key technological relevance [9]. Improving the electrical contact resistance [10], we demonstrated 10 nm transistors using *monolayer* MoS_2, with the highest current reported to date (>400 μA/μm), approaching ballistic limits [11]. Using Raman thermometry, we uncovered low thermal boundary conductance (~15 $MW/m^2/K$) between MoS_2 and SiO_2, which could limit heat dissipation in 2D electronics [12]. We are presently exploring unconventional applications including thermal transistors [13], which could enable nanoscale control of heat in "thermal circuits" analogous with electrical circuits. Overall, these studies reveal fundamental limits and new applications that could be achieved with 2D materials, taking advantage their unique properties.

References: **[1]** V. Dorgan, M.-H. Bae, E. Pop, *Appl. Phys. Lett.* 97, 082112 (2010). **[2]** M. Yamoah, et al., *ACS Nano* 11, 9914 (2017). **[3]** M.-H. Bae et al., *Nature Comm.* 4, 1734 (2013). **[4]** S. Islam, et al., *IEEE Electron Device Lett*. 34, 166 (2013). **[5]** A. Behnam et al., *Appl. Phys. Letters*. 107, 123508 (2015). **[6]** N. Wang et al., *IEEE VLSI Tech. Symp*., Jun 2016, Honolulu HI. **[7]** K. Smithe et al., *ACS Nano* 11, 8456 (2017). **[8]** M. Mleczko et al., *ACS Nano* 10, 7507 (2016). **[9]** M. Mleczko, E. Pop, et al., *Science Adv.* 3, e1700481 (2017). **[10]** C. English et al., *Nano Lett*. 16, 3824 (2016). **[11]** C. English et al., *IEEE Intl. Electron Devices Meeting (IEDM)*, Dec 2016. **[12]** E. Yalon, E. Pop, et al., *Nano Lett.* 17, 3429 (2017). **[13]** A. Sood, E. Pop et al. *in press* (2018).

Applied Surface Science Division
Room 204 - Session AS+BI-TuM

Applied Surface Science: From Electrochemistry to Cell Imaging, a Celebration of the Career of Nicholas Winograd

Moderators: Arnaud Delcorte, Université Catholique de Louvain, Belgium, Michaeleen Pacholski, The Dow Chemical Company

8:00am **AS+BI-TuM1 Surface Analysis and Beyond, Using Ion Beams and Lasers***, **Nicholas Lockyer**, J.C. Vickerman,* University of Manchester, UK **INVITED**

Applications of secondary ion mass spectrometry (SIMS) have expanded enormously from pure surface science experiments to biology and bio-medicine, driven largely by developments in instrumentation. Polyatomic primary ion beams have resulted in a step-change in the technique's capability to detect and localise molecular chemistry, in biological cells and organic devices etc. This has stimulated new mass spectrometer designs and analytical paradigms for molecular imaging in 2D and 3D. The quest for still greater lateral resolution is a quest for improved sensitivity. Here ion beam chemistry can play a role, increasing the ionized fraction of the sputtered plume. Alternative routes to improved ionization and greater quantification include laser post-ionization. In this talk I will chart the progress made in these areas by our group in Manchester, and draw parallels with the work of the Winograd group, with whom we have had fruitful collaboration over many years.

8:40am **AS+BI-TuM3 A High Resolution Tandem MS Imaging Method to Probe the Composition of Organelles in Single Cells***, **Gregory L. Fisher**,* Physical Electronics*; C.E. Chini,* University of Illinois at Urbana-Champaign*; B. Johnson, M.M. Tamkun,* Colorado State University*; M.L. Kraft,* University of Illinois at Urbana-Champaign

A goal of cellular imaging is to ascertain the composition of organelles, e.g. lipid profiling or pharmaceutical efficacy. To date most MS imaging of organelles is accomplished by stable isotope labeling because the imaging ion beam produces primarily (di)atomic ions. Such analyses are void of desired molecular specificity. We employed a TOF-TOF imaging capability [2] to achieve molecular specificity and conjectured that an ER-Tracker stain would yield characteristic molecular ions with which to image the endoplasmic reticulum (ER) and ER tubules.

We used human embryonic kidney (HEK) cells that had a high number of ER tubules near the plasma membrane (PM). Experimental cells were transfected to express GFP-Kv2.1 fluorescent ion channels. The cells were stained with ER-Tracker which selectively labels the ER. Control specimens were neither transfected nor stained.

We observed by simultaneous MS imaging and tandem MS imaging, in both the positive and negative ion polarities, the atomic and molecular moieties characteristic of an ER-Tracker stain localized to the ER and ER tubule structures. The ion species used for tandem MS imaging of the ER and ER tubules, namely F^-, $C_6H_5^-$, $C_5H_5^+$ and $C_{17}H_{15}N_2O^+$, were shown irrefutably via the product ion spectra to arise solely from the ER-Tracker stain. Two-dimensional (2D) imaging revealed intersection of some ER tubules at the PM. Three-dimensional (3D) visualization via depth profile analysis, carried out to a depth of ≈ 40 nm from the PM, revealed additional ER tubules just under the PM. Some ER-Tracker was observed in the PM indicating ER tubule contact with the PM to form ER-PM junctions. We were able to confirm the presence and position of the PM owing to the presence of characteristic lipids, lipid fragments and fatty acids which were imaged in parallel. The observed tubule features were imaged at an effective lateral resolution of 137 nm and had measured diameters in the range of approximately 500 nm to 2 μm corresponding well with previous studies [3] and present total internal reflection fluorescence (TIRF) observations. More than a dozen control cells were analyzed, and neither atomic nor molecular moieties characteristic of the ER-Tracker were observed to be present. Our next aim is to visualize the ER within entire cells and to assess the lipid composition at different locations within the ER. By extension, with organelle-specific stains, we can apply this TOF-SIMS tandem MS imaging method to aspects of pharmaceutical delivery and metabolism.

9:00am **AS+BI-TuM4 SIMS and MALDI-MS. Competitive, Complimentary or Complementary Techniques for Bio-imaging?**, ***John Stephen Fletcher***, *I. Kaya,* University of Gothenburg, Sweden

Despite imaging SIMS being a much older technique than MALDI in the bio-MS imaging area MALDI has enjoyed considerably more widespread success. The advantage of higher resolution imaging that is possible with SIMS has generally been outweighed by the low signal for intact molecular ions that are routinely delivered by soft ionisation techniques like MALDI – and MALDI is cheaper. However, advances in ion beams and mass spectrometry for SIMS analysis in parallel with new matrices, sample preparation and analysis approaches for MALDI have brought the two techniques closer together with significant overlap in the 1-10 µm "small molecule" imaging range.

In this presentation the benefits (if any) of multimodal MS imaging are discussed using examples from cancer, cardiovascular and neurological studies. Analysis was performed using high energy (40 keV) gas cluster ion beams (GCIBs) for SIMS analysis on the Ionoptika J105 and different MALDI approaches including gentle/static MALDI on the Bruker Ultraflextreme. On tissue derivatisation strategies applicable to both techniques will also be presented.

9:20am **AS+BI-TuM5 High Spatial Resolution Metabolic Imaging using the 3D OrbiSIMS - Fundamentals of Metabolite Fragmentation and Biological Applications**, *C. Newell, Y. Panina,* Francis Crick Institute, UK*; L. Matjacic, V. Cristaudo,* National Physical Laboratory, UK*; A.P. Bailey,* Francis Crick Institute, UK*; R. Havelund,* National Physical Laboratory, UK*; M. Yuneva, A.P. Gould,* Francis Crick Institute, UK*;* ***Ian S. Gilmore***, National Physical Laboratory, UK

Ground-breaking advances in single-cell genomics and transcriptomics are revealing the heterogeneity of cells in tissue and are transforming biological understanding. There is a great need for metabolomics with single-cell resolution. Recent advances in both SIMS and MALDI imaging have pushed the spatial resolution boundary to a few micrometres [1-3].

Here, we report on the 3D OrbiSIMS [1] which combines a gas cluster ion beam (GCIB) that is able to simultaneously achieve a spatial resolution of < 2 µm with high mass resolving power (>240 k) and mass accuracies of ~1 ppm. The GCIB significantly reduces fragmentation of metabolites compared with small cluster ion beams and we provide fragmentation data for a variety of metabolites for different energy per atom conditions.

We demonstrate the OrbiSIMS capability with two biological examples. Firstly, a study of the cuticular lipid composition and distribution of drosophila and how these change with various environmental and genetic manipulations. Drosophila secrete many different classes of lipids to form a protective surface barrier against environmental challenges and hydrocarbons which play a separate role as pheromones that influence sexual behaviour. Secondly, to identify metabolic heterogeneity in mammary gland tumours. One of the hallmarks of cancer is deregulated metabolism, often characterised by increased glucose and glutamine uptake for energetic and anabolic purposes. Metabolic changes contribute to well-established tumour heterogeneity, which is a major challenge for anti-cancer therapeutics. We demonstrate a protocol to co-register high-resolution OrbiSIMS metabolite images with immunohistochemistry microscopy images of the same sample.

References

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9:40am **AS+BI-TuM6 Small Molecule Imaging in Single Frozen-Hydrated Cells using High-Resolution Gas Cluster Ion Beam Secondary Ion Mass Spectrometry (GCIB-SIMS)**, ***Hua Tian***, *N. Winograd,* Pennsylvania State Univeristy

Cell heterogeneity leads to the development of antibacterial resistance and tumor relapses in response to drug treatment. Cell-to-cell differences have been extensively investigated at the DNA level. The study of rapid and dynamic small molecule fluctuations in single cells has lagged. However, the complete spectrum of biomolecules can be a direct indicator of cell phenotype and a reflection of immediate response to environment and chemical stress. There is currently no method to directly detect small molecules in their original state because of the rapid and dynamic nature of these molecules and impossibility of amplifying the metabolites. Previously, the characterization of drug and small molecules in cells are conducted using ensembles of cells, with which the spatial distribution, a vital piece for understanding biological processes is lost. The development of high resolution CCIB-SIMS in our lab has positioned us to directly image small molecule fluctuation in single cells under cryopreservation. The approach takes advantage of three aspects of GCIB-SIMS - low chemical damage, high yield of intact biomolecules, and the possibility of sub-micron lateral resolution. In this work, we utilize a DC beam buncher-ToF SIMS instrument to achieve high lateral resolution. Moreover, this configuration simplifies depth profiling since erosion and spectral acquisition are performed with a single beam. In addition, the flexibility of gas candidates for GCIB allows us to explore tailored beam for ionization enhancement, such as HCl, CH_4, CO_2 or H_2O (1~100%) doped Ar cluster beams. To illustrate this instrumental protocol, chemically resolved 3D images of single cells, HeLa cells and drug treated A549 (Carcinoma) and A673 (Ewing tumor) cells are imaged using a novel 70 keV $(CO_2)_{14000}+$ beam with a spot size of 1 µm. The stable intermediates from various biochemical pathways are visualized in single HeLa cells, demonstrating the sufficiency of the chemical sensitivity using GCIB. The drug propranolol is localized within the cellular structure of A673 and A549 cells, while no sign of fexofenadine is observed. This indicates that propranolol has high passive permeability in contrast to low passive permeability expressed by fexofenadine. Surprisingly, a lipid composition change is shown in A673 cells, particularly the depletion of phosphatidylinositol species after treatment. The approach provides a complete chemical picture of single cells at near original physiological and morphological state, opening the opportunities for single cell metabolomics and heterogeneity studies using SIMS.

11:00am **AS+BI-TuM10 Pushing the Limits of Measurement Science with SIMS**, ***Christopher Szakal***, *D.S. Simons, J.D. Fassett, T.P. Forbes,* National Institute of Standards and Technology (NIST) **INVITED**

The career of Dr. Nicholas Winograd was exemplified by an unwillingness to accept the scientific status quo. Both in words and actions, he set a tone that encouraged everyone he worked with to 'push the limits' of what they thought was possible within their research endeavors. In this presentation, several topics will be explored where this mindset has been directly put into practice. A mix of historical examples, recent advancements, and new science that fit within the theme will be presented. Specifically, topics related to cluster ion beams, single cell imaging, single cell quantification, precision isotopic measurements, secondary ion mass spectrometry (SIMS) standard generation, and precision atmospheric pressure ionization MS measurements will be described in terms of how the measurement science boundaries were assertively targeted. Since Dr. Winograd had a fondness for cutting-edge instrumentation throughout his career, the presented efforts will focus on pushing the limits within time-of-flight (TOF)-SIMS, large geometry (LG)-SIMS, and ultra-high-resolution (UHR)-MS quadrupole(Q)-TOF technologies.

11:40am **AS+BI-TuM12 Multiplexed Ion Beam Imaging: Cell and Tissue Imaging using Secondary Ion Mass Spectrometry for Pathology**, ***Jay Tarolli***, *R. Finck, M. Aksoy, D. Stumbo,* Ionpath, Inc.

Traditional techniques for protein imaging in tissue sections based on light microscopy are limited in the number of simultaneous targets that can be analyzed in a single sample. The need exists in pathology, however, for concurrent imaging of more than just a few of these biomolecules to determine localization of cell types in tissue biopsies. Multiplexed ion beam imaging (MIBI) uses secondary ion mass spectrometry (SIMS) to overcome these limitations and is capable of imaging over 40 biomolecules simultaneously with a spatial resolution greater than many traditional optical and fluorescence microscopy techniques.

In a typical MIBI analysis, a tissue sample is stained with target antibodies conjugated to isotopically pure lanthanide metals. The resulting mass spectra of monoatomic heavy metals exhibit a more characteristic response than the complex mass spectra of fragmented biomolecules typically acquired when analyzing tissue samples with SIMS, the benefit of which being twofold: First, as ion counts from the target analytes are preserved instead of lost due to fragmentation into uncharacteristic species, the generated images have a higher signal to noise ratio. Secondly, now that fragmentation of target analytes is not a limitation, a high current primary ion beam with a tight focus can be employed to image tissue samples with a high spatial resolution at a high throughput rate. Specifically, an oxygen duoplasmatron primary ion beam, focusable down to a spot size of 350 nm, is used in conjunction with a time-of-flight mass analyzer to enable to the simultaneous detection of more than 40 labels at a resolution where individual cells can be differentiated in tissue samples.

12:00pm **AS+BI-TuM13 Combined ToF-SIMS and AFM Protocol for Accurate 3D Chemical Analysis and Data Visualization**, ***Maiglid Andreina Moreno Villavicencio,*** *N. Chevalier, J.-P. Barnes, I. Mouton,* Univ. Grenoble Alpes, CEA, LETI, France*; F. Bassani,* Univ. Grenoble Alpes, CNRS, LTM, France*; B. Gautier,* Université de Lyon, INSA Lyon, Institut des Nanotechnologies de Lyon, UMR CNRS 5270, F- 69621 Villeurbanne cedex, France

In dual-beam time-of-flight secondary ion mass spectrometry (ToF-SIMS) depth profiling, a succession of two-dimensional chemical images is acquired. The provided images can be used to generate a three-dimensional (3D) visualization of the sputtered volume. However, standard reconstruction methods do not take into account the initial sample topography or lateral variations in sputter rates.

Due to geometry and the diversity of materials the resulting 3D chemical visualization of heterogeneous and non-planar samples may be distorted. To address this issue ToF-SIMS analysis was combined with atomic force microscopy (AFM). This combination supplies the missing sample topography of the ToF-SIMS images and allows the calculation of sputter rates for the materials present in the sample.

To achieve an accurate 3D ToF-SIMS reconstruction a protocol was developed that combines AFM topographical images, crater depth measurements and sequences of ToF-SIMS images, all acquired on the same area of the sample. This combined ToF-SIMS/AFM methodology was applied to a sample consisting of GaAs selectively grown in SiO_2 patterned structures using MOCVD. The initial topography revealed that the GaAs areas were higher than SiO_2 patterns, and the large sputter rate differences (up to a factor 2) mean that a simple reconstruction (flat surface and constant sputter rate) leads to severe distortions in the 3D ToF-SIMS reconstruction.

Using the combined methodology, a 3D overlay between AFM and ToF-SIMS images at each interface can be made and the local sputter rate can be mapped. Finally, a protocol was developed for the correction of the 3D ToF-SIMS reconstruction and depth-profiles within a rendered volume defined by successive AFM imaging.

This work was carried out on the nanocharacterisation platform (PFNC) of the CEA Grenoble and this project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 688225.

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Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-TuM

Nanochemistry in Heterogeneous Catalysis

Moderator: Matthew Marcinkowski, Pacific Northwest National Laboratory

8:00am **HC+SS-TuM1 Probing Oxide Supported Single Rh Atoms as Model Catalysts for CO Oxidation**, ***Alex C. Schilling***, *E.C.H. Sykes,* Tufts University

In recent years, single atom active sites have become a central topic in the creation of new catalysts with a focus on supported Rh atoms as a means of activating C-H bonds and catalyzing the water-gas shift reaction. These heterogeneous catalysts can operate at the single atom limit, decreasing the amount of precious metal on the support and thereby the price of the catalyst. However, debate still exists in the literature over the nature of the active sites and their mechanism of operation. We have taken a reductionist model study approach towards understanding these issues in well-defined single atom systems. Using surface-sensitive techniques, such as Temperature Programmed Desorption (TPD) and Reflection Absorption Infrared Spectroscopy (RAIRS), we assess the ability of single Rh atoms to oxidize CO. Experiments show that this system has the potential to convert the majority of Rh adsorbed CO to CO_2 at relatively low temperature. At low coverages of Rh (0.5-6%) preliminary experiments show two distinct desorption states for CO_2 at 325 K and 462 K. These TPD peaks account for 85% of all CO desorption from the Rh sites. The other 15% desorbs from Rh as CO at the same temperatures. Further work on this system will give insight into the nature of the active Rh sites, their interaction with both CO and support oxide, as well as the reaction mechanism.

8:20am **HC+SS-TuM2 Methanol Partial Oxidation Mechanisms on a Single-site Catalyst Pt_1/ZnO(10-10): A First-principles Study**, ***Tao Jiang,*** University of Central Florida*; T.B. Rawal,* Oak Ridge National Laboratory*; D. Le, T.S. Rahman,* University of Central Florida

The rational design of single metal atoms anchored on non-metallic surface has the great potential to offer catalysts with high activity and selectivity [1]. Towards this goal, we have carried out density functional theory based calculations of the catalytic behavior of singly dispersed Pt atoms on ZnO, Pt_1/ZnO(10-10), as a model system for methanol partial oxidation. We find that methanol adsorption is favored at the surface Zn site whereas oxygen prefers to adsorb at the Pt-Zn site. The adsorption of reaction intermediates CO, CO_2, and H_2 are favored at the Pt site, whereas H_2O prefers to sit at the Zn site. Secondly, along the reaction pathways for methanol dehydrogenation, we will illustrate that the O-H bond scission from methanol is slightly exothermic (ΔE=-13 meV). The resultant methoxy then preferentially adsorbs at the Pt-Zn site, where C-H bond of methoxy can be easily activated. The dissociation of methoxy (CH_3O' ' ->CH_2O+H) is exothermic (ΔE=-0.42 eV) and that of formaldehyde (CH_2O->' CHO+H) is endothermic (ΔE=+0.16 eV). The results suggest that Pt_1/ZnO(10-10) is a potential single-atom catalyst for methanol oxidation. We will compare our findings with those for the related system Pd_1/ZnO(10-10) [1] and available experimental observations to evaluate their relative advantages for methanol partial oxidation.

[1] T. B. Rawal, S. R. Acharya, S. Hong, D. Le, Y. Tang, F. F. Tao, and T. S. Rahman, submitted (2018).

The work is partially supported by DOE grants DE-FG02-07ER15842

8:40am **HC+SS-TuM3 Imaging the Ordering of Weakly Adsorbed CO_2 Molecules on Rutile Titania using Ambient Pressure Microscopy and Spectroscopy**, ***Rebecca Hamlyn***[1]*,* Brookhaven National Lab*; J.A. Rodriguez, S. Senanayake, M. Mahapatra, F. Xu, D. Grinter, S. Luo, P. Liu, R. Palomino, I. Waluyo, S. Kattel, D.J. Stacchiola,* Brookhaven National Laboratory

Recently, great effort has been devoted to the capture, activation and conversion of carbon dioxide (CO_2), a ubiquitous greenhouse gas and by-product of many chemical processes. The high stability and non-polar nature of CO_2 leads to weak bonding with well-defined surfaces of metals and oxides. The interactions of CO_2 involve intermolecular forces with noncovalent bonding (van der Waals), and often a surface needs to be functionalized to create polar sites that can "capture" or bind CO_2. Images from ambient pressure scanning tunneling microscopy show that a substantial amount of CO_2 can reside on a TiO_2(110) surface at room temperature as a consequence of weak bonding interactions with the substrate. Furthermore, the adsorbates exhibit a disorder-order transition on this surface, despite the lack of a strong interaction that may serve to impose its substrate periodicity on the adsorbed film. This phenomena is of interest to many areas of the surface science and chemistry community wherein condensation of van der Waals gases such as CH_4, N_2, or CO_2.

We have employed microscopic imaging under *in situ* conditions, soft X-ray spectroscopy and theory to decipher the unique ordering behavior seen for CO_2 on TiO_2(110).

9:00am **HC+SS-TuM4 Using Sn Atomic Layer Deposition to Tune the Coking Resistance of Size-selected Pt Model Catalysts**, ***Timothy Gorey***[2]*, E. Baxter, A. Cass, S. Anderson,* University of Utah*; B. Zandkarimi, A. Alexandrova,* University of California at Los Angeles

Size-selected cluster catalysts are powerful tools that enable us to probe and characterize specific catalytic reaction mechanisms controlled by the particle's size. By combining deposition of atomically-selected Pt clusters, with ALD to selectively add Sn atoms to the clusters, we obtain Pt-Sn alloy clusters with exactly known numbers of Pt atoms, and a narrow distribution of Sn atoms. In addition to being a powerful experimental tool, having size-selected model catalysts with well-defined compositions allow detailed theoretical simulations, providing insight into cluster structure, and the mechanistic origins of the size and alloying effects observed experimentally. It is found that tin alloying has a large and beneficial effect on both the branching between intact ethylene desorption vs. dehydrogenation/carbon deposition, and on the thermal stability of the clusters at temperatures to 700 K. Theoretical predictions for the structures

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[1] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

[2] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

and electronic properties of the thermally accessible ensemble of isomers are used to rationalize the observed effects in detail.

*Work supported by the United States Air Force Office of Scientific Research (AFOSR FA9550-16-1-0141)

9:20am **HC+SS-TuM5 Synergistic Effects of Pd and PdO Domains on Thin Film TbOx(111)/Pt(111)**, ***Christopher Lee***[1], *J.F. Weaver,* University of Florida

Among the rare earth oxides (REOs), the terbium oxides exhibit favorable properties in selective oxidation catalysis due to the flexibility in the storage and release of oxygen within the lattice. Of particular note is the ease of structural rearrangement into well-ordered intermediates between the Tb_2O_3 and TbO_2 stoichiometries, providing a novel, dynamic surface interface for the promotion of oxidation reactions. We investigated the stabilization and reactivity of metallic Pd domains grown on top of ultrathin c-Tb_2O_3(111)/Pt(111) films in ultrahigh vacuum (UHV) and subsequently oxidized by plasma-generated gaseous atomic oxygen. XPS shows that while both the film and metallic domains are almost fully oxidized to both TbO_{2-} and PdO by atomic oxygen, subsequent annealing to ~600 K can significantly reduce the TbO_x supporting film while leaving the PdO largely unreduced. Our results provide evidence that the presence of Pd structures on the TbO_x surface greatly promotes the thermal reduction of TbO_2. Further annealing of the system at ~900 K results in PdO decomposition and agglomeration of metallic Pd domains as evidenced by the diminution of the XPS Pd 3d peaks.

The oxidation/reduction behavior of the Pd/TbO_x(111) system has enabled the study of oxidative reactions on three characteristic interfaces: PdO on TbO_2(111), PdO on Tb_nO_{2n-m}(111), and Pd on c-Tb_2O_3(111). TPD and TPRS experiments show that adsorbed CO and C_3H_8 only react with the stabilized PdO domains, with C_3H_8 desorption at ~200 K being characteristic of adsorbed propane σ-complexes observed previously on PdO(101) surfaces. Continual reduction of PdO with adsorbed CO and C_3H_8 also show that when thermal reduction is limited to ~600 K, the underlying TbO_x support will continually replenish the reduced PdO domains with oxygen. This is also noted by the substantially higher conversion of adsorbed CO to CO_2 compared with that seen on pure PdO(101) as conversion would be less limited if reactive oxygen is supplied from both PdO and the TbO_x support. This behavior suggests a strong synergy between the surface Pd/PdO domains and the underlying TbO_x film, such as a Mars-van Krevelen interaction in which TbO_x readily transfers O-atoms to Pd and thereby sustains oxidation chemistry.

9:40am **HC+SS-TuM6 Copper Vapor Adsorption Calorimetry on $HCa_2Nb_3O_{10}$(001) Nanosheets: Energetics and Adsorbate Structure**, ***Wei Zhang***[2], *J.E. Eichler,* 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 chemical bonding strength at such interfaces is of great interest. These strengths have been measured on single-crystal oxide films of a single metal element by metal vapor adsorption calorimetry in ultrahigh vacuum (UHV), but never before on mixed oxides of two or more metal elements, yet mixed oxides are often used as supports in catalysis with considerable improvement on various aspects of catalyst performance. The preparation of atomically-smooth single-crystal mixed-oxide films in well-defined composition that would be applicable in our adsorption calorimetry is very challenging. Mallouk et. al. have reported a class of lamellar $HCa_2Nb_3O_{10}$(001) nanosheets which can be deposited in a layer-by-layer fashion on flat substrates using Langmuir-Blodgett (LB) techniques to make thin and well-ordered mixed-oxide films. These nanosheets can extend laterally for long distances (>1 µm) indicating that they have very high surface area with homogeneous surface sites and a huge ratio of terrace sites to sheet-edge sites. Furthermore, when used as supports for transition metal oxide (or hydroxide) nanoparticles, they display unusual stability against sintering. Here, we apply the surface chemistry techniques derived for single-crystal oxide films to the much more complex perovskite mixed-oxide films by investigating the adsorption of Cu atoms on the $HCa_2Nb_3O_{10}$(001) nanosheets (~6.3 nm thick) at both 300 K and low temperature (<150 K). Cu atoms show an initial heat of 186 kJ/mol at 300 K, which is close to the DFT value for Cu monomers. The heat of adsorption then increases quickly to the heat of sublimation of bulk Cu(s) (337 kJ/mol). Low-energy He^+ ion scattering spectroscopy (LEIS) allows us to investigate the morphology and the number density of Cu particles. The possible chemical reactions between the Cu atoms and the $HCa_2Nb_3O_{10}$(001) nanosheets during adsorption are elucidated using X-ray photoelectron spectroscopy (XPS).

11:00am **HC+SS-TuM10 Adsorption and Adhesion of Ni on MgO(100) at 300 and 100 K by Calorimetry**, ***Zhongtian Mao****, W. Zhao, Z. Almualem, C.T. Campbell,* University of Washington

Metal nanoparticles anchored on the surface of oxide support form the basis of modern heterogeneous catalysts used for clean energy, pollution prevention and industrial-scale chemical production. Since the catalytic activity, selectivity and long-term stability of supported nanoparticles correlate with metal chemical potential which in turn decreases strongly with the metal/oxide interface adhesion energy, E_{adh}, it is crucial to understand how the properties of both metal and oxide control E_{adh}. Adhesion energies of metal nanoparticles to clean oxide surfaces were previously measured in ultra-high vacuum using either single-crystal adsorption calorimetry (SCAC) or particle-shape measurements by electron microscopy or grazing-incidence X-ray scattering. The results reveal a trend that E_{adh} on a given oxide surface increases linearly from metal to metal with increasing metal oxophilicity, defined as the magnitude of the heat of formation of the most stable oxide from gas-phase metal atoms.[1] The oxophilicity of Ni is so high that it is predicted by this trend to have 50% higher adhesion than any of the other metals that have been studied on MgO(100) (i.e., Pb, Ag, Au, Pd Cu and Pt). We report here caloriometric heats of adsorption of Ni gas onto MgO(100) which validate this prediction and thus prove the predictive ability of this trend. Oxide-supported Ni nanoparticles are widely used as industrial catalysts, so these results are of interest in catalysis research. The adsorption of Ni vapor onto MgO(100) films grown on Mo(100) is studied at 300 and 100 K using single crystal adsorption calorimetry. The Ni particle morphology is investigated using He^+ low-energy ion scattering spectroscopy (LEIS) and X-ray photoelectron spectroscopy (XPS). Combining the heat of adsorption and this information on Ni particle morphology also allows the adhesion energy of Ni(solid) to MgO(100) to be found. The initial heat of adsorption at 300 K is 276.5 kJ/mol, 35.7 % lower than the saturation heat at high coverage (equal to the bulk heat of Ni sublimation). This initial heat corresponds to making Ni cluster that are ~0.53 nm in diameter. We also report the chemical potential of Ni versus particle size on MgO(100).

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11:20am **HC+SS-TuM11 *In situ* Microscopy of Oxide Growth and Transformation under Reaction Conditions**, ***Jan Ingo Flege***, University of Bremen, Germany **INVITED**

Current research in heterogeneous catalysis aims to provide a deeper understanding of all the components in a real catalytic system, which depending on the conditions typically comprises both metals and oxides in nanoparticulate form. Significant progress has been achieved by studying carefully devised model systems that facilitate detailed investigation of the structure and chemistry of the individual constituents in controlled environments. While traditional approaches have focused on the role of oxide-supported metal nanoparticles, in the so-called inverse configuration a nanosized metal oxide is supported on a transition metal, thereby allowing us to assess the properties of the nanoscale metal oxide and its defect chemistry as well as to gain complementary access to the oxide-metal interface.

In this presentation, we will focus on the epitaxial growth of ultrathin metal oxide films and nanostructures on transition metals, with a special emphasis on rare-earth oxides. These materials have attracted considerable attention owing to their rich chemistry and enhanced reducibility in proximity to transition metals. We will demonstrate that real-time monitoring of their synthesis under vacuum conditions as well as their structural and chemical modifications on the nanometer scale in reactive gaseous environments is possible using low-energy electron microscopy and related methods [1]. Primary examples will address reversible structural transformations in ruthenium, platinum, and copper supported cerium oxide inverse model catalysts [2-5] upon thermal and chemical reduction, e.g., from CeO_2 via the cubic Ce_2O_3 phase to hexagonal Ce_2O_3, concomitant with partial dissolution of the cerium oxide particles and considerable dispersion of metallic cerium on the substrate, resulting in irreversible morphological changes. Similar sesquioxide and dioxide phases are present directly after deposition of praseodymium oxide on the Ru(0001) surface [6, 7], illustrating an intrinsic nanoscale complexity and the importance of the oxide-metal interface.

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[1] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

[2] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

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Industrial Physics Forum
Room 101B - Session IPF+AS+BI+MN-TuM

Advanced Imaging and Structure Determination of Biomaterials

Moderators: David G. Castner, University of Washington, Michael Grunze, Max Planck Institute for Medical Research

8:00am **IPF+AS+BI+MN-TuM1 Chemical Imaging as a Tool to asses Molecular and Morphologic Content in Natural Tissues and Fabricated Models***, R. Bhargava, T. Comi, M. Gryka, **Kevin Lee Yeh**,* University of Illinois at Urbana-Champaign **INVITED**

Chemical imaging, in which molecular content is obtained using spectroscopy and images are formed using microscopy, is an emerging area to characterize cells and tissues. We present here a chemical imaging approach based on mid-infrared spectroscopic imaging that combines the spatial specificity of optical microscopy with the molecular selectivity of vibrational absorption spectroscopy. IR spectroscopic imaging is particularly attractive for the analysis of cells and tissue in that it permits a rapid and simultaneous fingerprinting of inherent biologic content, extraneous materials and metabolic state without the use of labeled probes. Recorded data are related to the structural and functional state of the biological material using computation. We describe the computational strategy and statistical considerations underlying decision-making for this modality. A combination of theory, novel instrumentation and signal processing forms an integrated approach to biochemical analyses. First, we describe attempts to automate histopathology without dyes or human input. Results indicate that a rapid assessment of tissue is possible. Applied to engineered 3D tissue models for breast tumors, we show that the imaging technology is useful in rapidly assessing culture quality and that the model systems can act to inform researchers about the involvement of different cell types in cancer progression. Finally, we integrate imaging observations with those from conventional biological experiments to provide a complete view of cancer progression in these systems.

8:40am **IPF+AS+BI+MN-TuM3 Fluorescence Dynamics and Nonlinear Optical Imaging Methods for Biomedical Applications***, **Alba Alfonso Garcia**, L. Marcu,* University of California at Davis **INVITED**

Generation of quality bioengineered tissue constructs, a main cornerstone for regenerative medicine, require new tools to monitor their maturation processes. Optical imaging, and in particular fluorescence dynamics and nonlinear optical techniques, provides the means for non-destructive, longitudinal, and quantitative evaluation. Using fiber optics and catheterized imaging systems these strategies are implemented with flexible geometries that allow investigations be performed outside of the realm of the microscope and the microscope slide, but instead *in situ*, on bioreactors, culturing wells and chambers, or even *in vivo*. Fluorescence dynamics and nonlinear optical imaging are especially well suited as they rely on intrinsic properties of the biomaterials to generate contrast. Tissue autofluorescence allows spectroscopic evaluation of tissue components, and the analysis of its temporal dynamics leads to functional analysis of tissue status. Additionally, nonlinear light-matter interactions probe vibrational and electronic energy levels that provide enhanced biochemical specificity of tissue constituents. All these approaches are compatible with label-free strategies, avoiding the addition of labeling agents onto already complicated samples. In this presentation, I will overview applications of fluorescence dynamics and nonlinear optical imaging including fluorescence lifetime imaging, two-photon fluorescence or second harmonic generation in tissue engineering. In particular, I will discuss tracking approaches to visualize recellularization processes on bioengineered vascular constructs. I will also characterize tissue composition of carotid arteries along their length based on their autofluorescence lifetime signals, and how this correlate with the structural protein composition of the vessel wall as evaluated by gold-standard biochemical assays. Finally, we will see how these methods are also applied in different fields such as the generation of cartilage-based implants, and the real-time discrimination of healthy versus diseased tissues in the context of cancer diagnostics.

9:20am **IPF+AS+BI+MN-TuM5 Single Molecule Imaging of Receptor Signalling***, **Katharina Gaus**,* University of New South Wales, Australia **INVITED**

Antigen recognition by the T cell receptor (TCR) is a hallmark of the adaptive immune system. When the TCR engages a peptide bound to the restricting major histocompatibility complex molecule (pMHC), it transmits a signal *via* the associated CD3 complex. How the extracellular antigen recognition event leads to intracellular phosphorylation remains unclear.

We develop single-molecule localization microscopy (SMLM) apporaches and novel analysis to determine how spatial organization regulates signal initiation and propagation. For example, we used SMLM data to map the organization of TCR-CD3 complexes into nanoscale clusters and to distinguish between triggered and non-triggered receptor copies. We found that only TCR-CD3 complexes in dense clusters were phosphorylated and associated with downstream signaling proteins, demonstrating that the molecular density within clusters dictates signal initiation. This lead us to propose a model in which antigen recognition is first translated into receptor clustering and then the density of receptor nanoclusters is translated into signaling. This model may explain how T cells can respond to both the affinity and dose of pMHC molecules with a common signal transduction mechanism (Pageon et al. PNAS 2016). We also developed novel FRET sensors to monitor the rate of receptor clustering (Ma et al. Nat Commun 2017) and a sensor that reports membrane charges (Ma et al. Nat Biotech 2017) to understand how biophysical properties of the plasma membrane contribute to TCR signaling.

11:00am **IPF+AS+BI+MN-TuM10 Developing a Google-earth View of Tumour Metabolism through Multiscale Molecular Imaging***, J. Bunch, **Rory T. Steven**,* National Physical Laboratory, UK **INVITED**

Mass spectrometry (MS) is one of the most powerful techniques for chemical analysis and when combined with an imaging modality allows molecular chemistry to be visualised in 2D and 3D, from the nano- to the macroscale, in ambient conditions and in real-time. There are numerous techniques each having different modes of operation including label-free and labelled analyses.

Cancer Research UK has identified that building an understanding of the inter- and intra- heterogeneity of tumours and their evolution over time and in response to therapy will require greater insight into the underlying biology, using *in vivo* and *in vitro* models and integrating biomarkers into both early- and late-phase trials. In 2017 the Grand Challenge programme was launched. Our collaborative action involves NPL, Imperial College London, The Beatson Institute, ICR, Barts Cancer Institute, The Francis Crick Institute, The University of Cambridge and AstraZeneca. Together we will develop a validated pipeline for multi-scale imaging of tumours collected from GEMMs and patients.

By pursuing a multiscale (organ to organelle) and multi-omics approach with a range of mass spectrometry imaging (MSI) techniques (MALDI, DESI, SIMS and ICP MS), we aim to deepen our understanding of the interplay of genes, proteins, metabolites and the role of the immune system in cancer development and growth.

This presentation will review early results and a discussion of the challenges associated with such a large, multi-technique, multi-site, mass spectrometry project.

11:40am **IPF+AS+BI+MN-TuM12 X-ray Diffraction and Coherent Imaging with Nano-focused Radiation: A Multi-scale Approach from Biomolecular Assembly to Cell, Tissue and Organ***, **Jan-David Nicolas**, T. Salditt,* University of Göttingen, Germany **INVITED**

X-rays deeply penetrate matter and thus provide information about the functional (interior) architecture of complex samples, from biological tissues and cells to novel composite materials. However, this potential of hard x-rays in view of penetration power, high spatial resolution, quantitative contrast, and compatibility with environmental conditions has to date not been fully developed, mainly due to significant challenges in x-ray optics. With the advent of highly brilliant radiation, coherent focusing, and lensless diffractive imaging this situation has changed. We show how nano-focused hard x-rays can be used for scanning as well as for full field holographic x-ray imaging of biological samples [1]. The central challenge of inverting the coherent diffraction pattern will be discussed and different reconstruction algorithms will be presented, from holographic techniques [2] to ptychography [3,4]. Next, we will present new approaches to treat the massive diffraction data recorded in scanning nano-diffraction experiments of cells and tissues [5].

By scanning the sample through the focused x-ray beam and recording full diffraction patterns in each scan point, structural parameters can be mapped throughout the cell or histological section [6], offering a 'diffraction contrast' by which one can localize also unstained biomolecular assemblies in cells and tissues, and at the same time investigate their structure. As an example, we address the sarcomeric organization in heart muscle cells (cardiomyocytes) [7,8], and show how the sarcomere organization evolves and differs between different cell types and maturation states. As a multi-scale approach, we then discuss sarcomeric structure in heart tissue sections, and then finally present phase contrast tomography reconstructions of an entire mouse heart.

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Materials and Processes for Quantum Computing Focus Topic
Room 203A - Session MP+EM+NS-TuM

High Coherence Qubits for Quantum Computing

Moderator: Robert Ilic, National Institute of Standards and Technology

8:00am **MP+EM+NS-TuM1 MBE Grown Nitride Superconductors for Quantum Circuits***, **Christopher Richardson**, A. Alexander, C. Weddle,* Laboratory for Physical Sciences

Low microwave loss superconducting capacitors and inductors are critical circuit components of superconducting qubits. For transmon qubits, the ability to make high-quality planar resonators is an essential part of fabricating highly coherent qubits. Plasma assisted Molecular beam epitaxy (PAMBE) is used to grow niobium titanium nitride alloys ($Nb_xTi_{1-x}N$) directly on silicon (111) wafers. Using a structure first approach to design optimization, the structural, surface topology, chemical characteristics, and superconducting critical temperature of these films are used for optimization of the growth conditions before resonators are fabricated and tested. Here focus will be on the optimization of PAMBE-TiN films grown under slightly nitrogen rich conditions and high growth temperatures. Using films grown on high resistivity wafers, resonators are fabricated from coplanar waveguides with a narrow 6-µm wide center conductor and nominal 500-nm deep trench etch. Cryogenic testing at 100mK demonstrate low microwave loss that is evident from measured internal quality factors that are over 1M in the single photon regime and approach 10M at high powers. The motivation of using PAMBE to grow superconductors and the favorable comparison with resonators made from leading films synthesized with sputter deposition will also be discussed.

8:20am **MP+EM+NS-TuM2 Towards Improved Coherence Times in Transmon Qubits***, **Sam Stanwyck**,* Rigetti Computing

The depth of the circuit a quantum computer can perform depends directly on the coherence times of its qubits. There are many sources of decoherence in superconducting qubits, and identifying and minimizing dominant sources is a critical step in improving the performance of quantum computers. By measuring the internal quality factor of resonators and deliberately coupling to different loss mechanisms, we identify dominant sources of resonator loss in our systems, as well fabrication process changes to ameliorate these losses. Additionally, defects and materials present on the chip surface are correlated with process changes and coherence metrics.

8:40am **MP+EM+NS-TuM3 Design and Fabrication for High Coherence Quantum Circuits***, **David Pappas**, X. Wu, R. Lake, M. Bal, J. Long, C.R. McRae, H.S. Ku,* National Institute of Standards and Technology (NIST) **INVITED**

In this talk we focus on achieving high coherence in multi-component quantum circuits [1,13]. We will discuss geometric and electrical design strategies that mitigate energy loss while maintaining sufficient coupling to the qubit. Materials considerations -including dielectric losses in the substrate and various interfaces -play a central role in the implementation of these circuits. We will present a summary of our studies of the various participation factors and processing techniques to reduce dielectric loss in the capacitance of the qubits and resonators for readout and coupling. We also review our methods of integration for the key nonlinear component, the overlap tunnel junctions. In particular, techniques for achieving smooth surfaces for the junctions in a back-end process will be shown.

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9:20am **MP+EM+NS-TuM5 Effect of Surface Treatment on Superconducting Qubit Coherence***, **Bradley Christensen**,* University of Wisconsin-Madison*; P. Kumar,* University of Wisconsin - Madison*; J.J. Nelson, Y. Liu, A. Ballard, B.L.T. Plourde,* Syracuse University*; R. McDermott,* University of Wisconsin - Madison

Superconducting qubits are an attractive candidate for quantum information processing in the solid state . The fidelity of two-qubit gates for superconducting qubits is one of the more challenging limitations toward scalable quantum computing. A promising approach to perform these gates uses flux-tunable qubits to bias the qubit pairs into resonance to perform the necessary entangling operations. While this approach has many advantages over competing techniques, there are still significant issues that limit the fidelity of the gates. For example, since the two-qubit gate requires flux-biasing of a qubit, this also necessarily requires one of the qubits to operate at a flux-sensitive point, and as such, 1/f flux noise will restrict the possible gate fidelity. In addition to flux noise, flux-tunable qubits also suffer from microscopic two-level system (TLS) defects that reside in the high field areas on the qubit capacitor pad. These TLS cause an enhanced decay through both resonant interactions with the qubit and Landau-Zener transitions as the qubit frequency is biased through a TLS. While one could perform spectroscopy of the TLS to map out the inoperable space, this becomes an inefficient solution for large scale systems as the TLS resonance frequencies are not stable, and will significantly drift over time.

Recent experiments on SuperconductingQUantum Interference Devices (SQUID) point to adsorbed molecular O_2 as the dominant contributor to magnetism in superconducting thin films, and demonstrate that improvements in the sample vacuum environment lead to significant reductions in surface spin susceptibility and magnetic flux noise power. Furthermore, TLS defects have been shown to reside in surface oxides and interfaces, where the TLS dipole couples to the qubit electric field, and experiments on microwave resonators have shown that high-temperature annealing can yield a reduction in surface TLS defects.

Here, we present our results on improving the vacuum environment of superconducting qubits with an ultra-high vacuum (UHV) bake to remove the adsorbates. We measure flux noise power spectral densities (PSD) using Ramsey-based, CPMG filtering, and dressed-dephasing techniques, allowing the flux PSD measurements to span 10 decades. Furthermore, by measuring qubit lifetime as a function of frequency (swap spectroscopy), we can map out the coupling strength, lifetime, and density of the TLS defects. We present a comparison of treated and untreated devices to demonstrate the improvement to qubit coherence through a UHV bake.

9:40am **MP+EM+NS-TuM6 Metrology of Dielectric Loss using Lumped-Element Microwave Resonators***, **Corey Rae McRae**, X. Wu, M. Bal, J. Long, H.S. Ku, D.P. Pappas, R. Lake,* National Institute of Standards and Technology

Reducing the overall concentration of TLSs in dielectric materials remains at the forefront of materials research in quantum information science. In this work, we measure a lumped element resonator fabricated from a superconductor-dielectric-superconductor trilayer to determine the TLS loss of various dielectrics of interest in superconducting quantum computing. The deposition of the trilayer prior to fabrication allows control of the metal-dielectric interfaces, and the fabrication process is generalized so that resonators containing different dielectrics can be compared easily. This lithography method enables the measurement of trilayer capacitors and junctions that have been prepared entirely in situ in an ultrahigh vacuum environment. In future work, we will interrogate a new class of low-loss dielectrics grown with epitaxial methods using the measurement capabilities developed here.

11:00am **MP+EM+NS-TuM10 Direct Observation of Atomic Structure of Ultra Thin AlO_x Barriers in $Al/AlO_x/Al$ Josephson Junctions for Quantum Devices***, **Eva Olsson**,* Chalmers University of Technology, Gothenburg, Sweden **INVITED**

The atomic structure of tunnel barriers in Josephson junctions for quantum devices and the corresponding interfaces determine the properties of the junction. The thinnest region in the barrier of a junction will be the preferential tunneling channel for charge carriers and the highest current. The current increases exponentially with decreasing barrier thickness. As a consequence, a variation on the individual atom plane length scale results in inhomogeneity of the tunnel current across the barrier. There are several earlier experimental indirect indications that only a small fraction of the junction area is active.

We are using high resolution annular dark field (ADF) scanning transmission electron microscopy (STEM) imaging to obtain high resolution (better than 1 Å) and high precision (better than 1 pm) information about the local atomic structure [1]. We use ADF STEM imaging to directly determine the thickness distribution along the oxide barrier in $Al/AlO_x/Al$ Josephson junctions [2]. The barrier thickness is about 1-2 nm. The thickness distribution shows that less than 10% of the junction area dominates the electron tunneling. We also study the influence of oxygen pressure and oxidation time on the thickness distribution. In addition, we determine the atomic structure and coordination of Al atoms within the oxide barrier layer using electron energy loss spectroscopy and nanobeam electron diffraction [3]. A lower Al coordination is observed at the metal/oxide interface compared to the interior of the oxide barrier. We also study the structure of the interfaces between the Al contact and the substrate [4,5].

[1] A.B. Yankovich, R. Verre, E. Olsen, A.E.O. Persson, V. Trinh, G. Dovner, M. Käll and E. Olsson, ACS Nano 11 (2017) 4265.

[2] L.J. Zeng, S. Nik, T. Greibe, P. Krantz, P. Delsing and E. Olsson, J. Phys. D: Appl. Phys.48 (2015) 395308

[3] L.J. Zeng, D.T. Tran, C.-W- Tai, G. Svensson and E. Olsson, Sci. Rep. 6 (2016) 29679.

[4] L.J. Zeng, T. Greibe, S. Nik, C.M. Wilson, P. Delsing and E. Olsson, J. Appl. Phys. 113 (2013) 143905

[5] L.J. Zeng, P. Krantz, S. Nik, P. Delsing and E. Olsson, J. Appl. Phys. 117 (2015) 163915.

11:40am **MP+EM+NS-TuM12 Metrology of Tunnel Junctions for Superconducting Qubits***, **Russell Lake**,* National Institute of Standards and Technology (NIST)*; X. Wu, H.S. Ku, J. Long, M. Bal, C.R. McRae,* National Institute of Standards and Technology (NIST) and University of Colorado Boulder*; D.P. Pappas,* National Institute of Standards and Technology (NIST)

Superconducting tunnel junctions make up the key non-linear circuit component in many implementations of quantum electrical circuits, including superconducting qubits. Therefore, controllable fabrication of superconducting junctions has taken a central role in the realization of quantum computers. In this talk we discuss fabrication and characterization of a wafer-scale process for nanoscale superconducting tunnel junctions (Al-AlOx-Al) [1]. We present the distribution of normal-state resistances across a wafer for different junction sizes. We have applied an analytical method of accounting for the current crowding in the junction leads [2] in order to give accurate predictions of the supercurrent from the room-temperature raw data. These corrected resistances can be input into the Ambegaokar-Baratoff formula to predict the critical current of the tunnel junctions in the superconducting state [3], and the corresponding non-linear effective inductance. These results are immediately relevant to the task of qubit frequency allocation in multi-qubit systems.

[1] Appl. Phys. Lett. **111**, 032602 (2017); https://doi.org/10.1063/1.4993937

[2] J. Appl. Phys. **105**, 094503 (2009); https://doi.org/10.1063/1.3122503

[3] Phys. Rev. Lett. **10**, 486 (1963) and **11**, 104 (1963); https://doi.org/10.1103/PhysRevLett.10.486

Manufacturing Science and Technology Group
Room 202B - Session MS+MI+RM-TuM

IoT Session: Challenges of Neuromorphic Computing and Memristor Manufacturing (8:00-10:00 am)/Federal Funding Opportunities (11:40 am-12:20 pm)

Moderators: Christopher L. Hinkle, University of Texas at Dallas, Sean Jones, National Science Foundation (NSF), Alain C. Diebold, SUNY Polytechnic Institute

8:00am **MS+MI+RM-TuM1 ReRAM – Fabrication, Characterization, and Radiation Effects***, **David Hughart**, R.B. Jacobs-Gedrim, K.E. Knisely, N.J. Martinez, C.D. James, B.L. Draper, E.S. Bielejec, G. Vizkelethy, S. Agarwal,* Sandia National Laboratories*; H.J. Barnaby,* Arizona State University*; M.J. Marinella,* Sandia National Laboratories **INVITED**

Resistive switching properties in transition metal oxides and other thin films have been an active area of research for their use in nonvolatile memory systems as Resistive Random Access Memory (ReRAM). ReRAM is a candidate for storage class memory technologies, and studies have also revealed a high degree of intrinsic radiation hardness making digital ReRAM a candidate for radiation-hardened memory applications. Analog ReRAM has also generated interest from the neuromorphic computing community for use as a weight in neural network hardware accelerators.

One of the manufacturing challenges for the valence change memory (VCM) type of ReRAM has been the development of substoichiometric switching layer films. Physical vapor deposited (PVD) substoichiometric TaO_x films are an attractive option for a VCM switching layer because they are complementary-metal-oxide-silicon (CMOS) compatible and are deposited at low temperatures. However, control of the oxygen partial pressure to produce substoichiometric TaO_x films cannot be directly achieved through flow control because the oxygen consumption by the Ta target and chamber surfaces is nonlinear as the chamber transitions from metal to insulator conditions. The oxygen partial pressure can be controlled using a feedback system, though feedback-assisted deposition techniques are difficult to regulate, making them ill-suited to production. One alternative to a feedback system is to deposit a higher stoichiometry TaO_x film, deposited in a more stable flow-partial pressure chamber regime, and use annealing to drive Ta into the film to achieve the desired stoichiometry. Here, we compare switching layers fabricated using both techniques, and discuss the relative merits of each technique. The devices are manufactured in crossbar arrays to be testable by automatic probers, enabling the collection of large scale yield and performance data sets across process splits.

Manufacturing improvements enabled fabrication of analog ReRAM with characteristics suitable for neuromorphic computing applications. The performance of a TaO_x ReRAM based hardware accelerator at image classification accuracy after training was evaluated. The classification accuracy showed little degradation in initial radiation tests, suggesting analog ReRAM may be suitable for neuromorphic computing applications in radiation environments as well.

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8:40am **MS+MI+RM-TuM3 Memristive Synapses – Tuning Memristors for Performance and CMOS Integration***, **Nathaniel Cady,*** SUNY Polytechnic Institute **INVITED**

Neuromorphic computing systems can achieve learning and adaptation in both software and hardware. The human brain achieves these functions via modulation of synaptic connections between neurons. Memristors, which can be implemented as Resistive Random Access Memory (ReRAM), are a novel form of non-volatile memory expected to replace a variety of current memory technologies and enable the design of new circuit architectures. Memristors are a prime candidate for so-called "synaptic devices" to be used in neuromorphic hardware implementations. A variety of challenges persist, however, for integrating memristors with CMOS, as well as for tuning device electrical performance. My research group has developed a fully CMOS-compatible integration strategy for ReRAM-based memristors on a 300 mm wafer platform, which can be implemented in both front-end-of-line (FEOL) and back-end-of-line (BEOL) configurations. With regard to memristor performance, we are focusing on strategies to reduce stochastic behavior during both binary and analog device switching. This is a key metric for neuromorphic applications, as variability in device conductance state directly influences the ultimate number of levels (weights) that can be implemented per synapse. Using a two pronged approach, we have developed device operational parameters to maximize analog performance, while also tuning the ReRAM materials stack and processing conditions to reduce stochasticity and optimize switching parameters (forming, set, and reset).

9:20am **MS+MI+RM-TuM5 Analog In-Memory Computing for Deep Neural Network Acceleration***, **Hsinyu Tsai,** S. Ambrogio, P. Narayanan, R.M. Shelby, G.W. Burr,* IBM Almaden Research Center **INVITED**

Neuromorphic computing represents a wide range of brain-inspired algorithms that can achieve various artificial intelligence (AI) tasks, such as classification and language translation. By taking design cues from the human brain, such hardware systems could potentially offer an intriguing Non-Von Neumann (Non-VN) computing paradigm supporting fault-tolerant, massively parallel, and energy-efficient computation.

In this presentation, we will focus on hardware acceleration of large Fully Connected (FC) DNNs in phase change memory (PCM) devices [1]. PCM device conductance can be modulated between the fully crystalline, low conductance, state and the fully amorphous state by applying voltage pulses to gradually increase the crystalline volume. This characteristic is crucial for memory-based AI hardware acceleration because synaptic weights can then be encoded in an analog fashion and be updated gradually during training [2,3]. Vector matrix multiplication can then be done by applying voltage pulses at one end of a memory crossbar array and accumulating charge at the other end. By designing the analog memory unit cell with a pair of PCM devices as the more significant weights and another pair of memory devices as the less significant weights, we achieved classification accuracies equivalent to a full software implementation for the MNIST handwritten digit recognition dataset [4]. The improved accuracy is a result of larger dynamic range, more accurate closed loop tuning of the more significant weights, better linearity and variation mitigation of the less significant weight update. We will discuss what this new design means for analog memory device requirements and how this generalizes to other deep learning problems.

1. G. W. Burr et al., "Experimental demonstration and tolerancing of a large-scale neural network (165,000 synapses), using phase-change memory as the synaptic weight element," IEDM Tech. Digest, 29.5 (2014).

2. S. Sidler et al., "Large-scale neural networks implemented with non-volatile memory as the synaptic weight element: impact of conductance response," ESSDERC Proc., 440 (2016).

3. T. Gokmen et al., "Acceleration of Deep Neural Network Training with Resistive Cross-Point Devices: Design Considerations," Frontiers in Neuroscience, 10 (2016).

4. S. Ambrogio et al., "Equivalent-Accuracy Accelerated Neural Network Training using Analog Memory," Nature, to appear (2018).

11:00am **MS+MI+RM-TuM10 Computation Immersed in Memory: Integrating 3D vertical RRAM in the N3XT Architecture***, **Weier Wan,** W. Hwang, H. Li, T.F. Wu, Y.H. Malviya,* Stanford University*; M.M.S. Aly,* Nanyang Technological University, Singapore*; S. Mitra, H.-S.P. Wong,* Stanford University **INVITED**

The rise of data-abundant computing, where massive amount of data is processed in applications such as machine learning, computer vision and natural language processing, demands highly energy-effcient computing systems. However, the limited connectivity between separated logic and memory chips in conventional 2D system results in majority of program execution time and energy spent at memory access.The Nano-Engineered Computing Systems Technology (N3XT) [1] approach overcomes these memory bottlenecks by monolithically integrating interleaving layers of memory and logic on the same chip, and leveraging nano-scale interlayer vias (ILVs) to provide ultra-dense connectivity between logic and memory.

The metal oxide resistive switching memory (RRAM) [2] offers non-volatility, good scalability, and monolithic 3D integration, making it a good candidate as on-chip high-capacity main memory and storage in the N3XT system. Our experimentally calibrated studies show that a N3XT system with RRAM as digital storage and CNFET as logic devices could achieve 2-3 orders of magnitude improvement in energy efficiency (product of execution time and energy) in a wide range of applications (e.g. PageRank, deep neural network inference) compared to a conventional 2D system. Such 3D nano-system has also been experimentally demonstrated with RRAM, CNFET and CMOS monolithically integrated to perform in-situ ambient gas classification [3] and hyper-dimensional computing [4].

Besides offering substantial benefits for conventional digital systems, the monolithic integration of RRAM and logic devices also enables "in-memory computing", where computation is performed in the memory itself without explicitly moving data between memory and logic. Various types of in-memory computing operations could be performed using RRAM arrays, including analog multiply-accumulate and bit-wise logical operations. We perform system modeling that models program scheduling, communication and routing, and memory array and its peripheral circuits design on various operations to study their benefits and bottlenecks from application level. In particular we analyze the in-memory vector-matrix multiplication for deep neural network inference and bit-wise operations in 3D vertical-RRAM for hyper-dimensional computing. We show that with algorithm-architecture co-design, RRAM-based in-memory computing could further improve energy and area efficiency compared to digital implementation in a 3D monolithically integrated system.

[1] M.M.S. Aly et al., IEEE Computer, 2015. [2] H.-S P. Wong et al., Proc. IEEE, 2012. [3] M.M. Shulaker et al., Nature, 2017. [4] T. Wu et al., ISSCC, 2018.

11:40am **MS+MI+RM-TuM12 Materials for the Second Quantum Revolution***, **Tomasz Durakiewicz,*** Los Alamos National Laboratory

Onset of the second quantum revolution is marked by proliferation of quantum technologies. Still mostly in the laboratory R&D phase, but likely to emerge soon as a growing sector of general consumer technology, quantum devices require constant supply of novel functional quantum materials. The current paradigm of meticulous long-term studies to understand fundamental properties in detail and be able to model them ab initio is unlikely to disappear; however, the rapid growth of technology may require modification of classical approach by accelerated discovery process aided by machine learning, data mining, and ability to model, synthesize and test novel materials quickly. In this presentation we will discuss opportunities and current developments in select classes of quantum materials, like low-dimensional materials, strongly correlated systems and topological insulators, and the role NSF plays in this rapidly growing area.

12:00pm **MS+MI+RM-TuM13 SynBio(medicine): The Intersection Biomaterials and Living Systems***, **David Rampulla,*** National Institute of Health

The National Institute for Biomedical Imaging and Bioengineering (NIBIB) has long supported the development of biomaterials as platform technologies with broad biomedical application and has recently started a program in Synthetic Biology. This presentation will discuss the biomaterials portfolio at NIBIB with a specific focus on the use of synthetic biology approaches to engineer next generation materials for biomedicine. The talk will also highlight specific funding opportunities of interest and discuss some strategies for navigating the NIH application process.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+AN+EM+MN+MP+RM-TuM

Nanophotonics, Plasmonics, and Metamaterials

Moderators: Alokik Kanwal, NIST Center for Nanoscale Science and Technology, Nikolai Klimov, National Institute of Standards and Technology

8:00am **NS+AN+EM+MN+MP+RM-TuM1 Parametric Nonlinear Interactions in Nanofabricated Silicon-based Photonics*, Amy Foster,*** Johns Hopkins University **INVITED**

High optical confinement waveguides on integrated platforms enable nonlinear optical interactions with low power levels. The third-order nonlinear susceptibility, a modification of a material's permittivity due to an applied optical field, exists in all materials, and is an intensity-dependent process leading to third-order parametric effects. Harnessing the high optical intensities enabled by high confinement waveguides allows standard semiconductor materials to become power-efficient parametric nonlinear optical devices that can operate with powers in the mW range. The optical confinement of a waveguide also enables control over the waveguide's dispersion, allowing for phase-matching of the parametric processes thereby improving its operating bandwidth. Using standard nanofabrication techniques, integrated photonic devices can be tailored in both geometry at the nanoscale, and in magnitude of their third-order susceptibility through modification of their material properties. In this talk, we will discuss a variety of parametric nonlinear optical demonstrations in silicon-based waveguides including optical parametric amplification and oscillation, phase-sensitive amplification, and frequency conversion and comb generation. Furthermore, we will discuss these devices for a variety of applications including optical signal processing, spectroscopy, and security.

8:40am **NS+AN+EM+MN+MP+RM-TuM3 Ultrafast Optical Pulse Shaping using Dielectric Metasurfaces*, Amit Agrawal,*** *S. Divitt, W. Zhu, C. Zhang, H.J. Lezec,* NIST Center for Nanoscale Science and Technology **INVITED**

Since the invention of femtosecond pulsed lasers, the field of ultrafast optical science and technology has seen significant progress in the generation and characterization of ultrashort optical pulses. Complimentary to development in generation and characterization techniques, arbitrary temporal shaping of optical pulses has become an integral part of the field. Fourier-transform pulse shaping is the most widely adopted approach that entails parallel modulation of spatially separated frequency components to achieve the desired pulse shape. Recently, dielectric metasurfaces have emerged as a powerful technology for arbitrary control over the amplitude, phase, or polarization of light in a single, compact optical element. Here, we experimentally demonstrate shaping of sub-10 fsec ultrafast optical pulses using a centimeter-scale silicon metasurface acting as both amplitude and phase modulation mask. The deep-subwavelength silicon nanostructures, positioned with nanometer precision, are individual optimized to provide accurate amplitude and phase modulations to each frequency component. Masks of this type offer a lower cost, larger size, higher resolution, high diffraction efficiency, high damage threshold method for controlling ultrafast pulses.

9:20am **NS+AN+EM+MN+MP+RM-TuM5 Single-Particle Nanophotonics and Materials Investigations with Optical Microresonator Spectrometers*, Erik Horak,*** University of Wisconsin - Madison*; K.D. Heylman, K.A. Knapper, M.T. Rea, F. Pan, L.T. Hogan, R.H. Goldsmith,* University of Wisconsin-Madison **INVITED**

Optical microresonators have achieved impressive sensitivities in a range of experimental modalities. We leverage the exquisite sensitivity of microresonators to enable highly sensitive spectroscopic characterization of objects on the surface of the resonator. In this way, not only can single particles be detected and identified, but fundamental properties of interrogated systems can be studied, opening a path to mechanistic studies and label-free chemical identification.

Our photothermal-based technique employs a two-beam geometry. A fiber-coupled (probe) beam records the whispering-gallery mode (WGM) resonance wavelength via evanescent coupling through a tapered fiber, while a second free-space (pump) beam heats absorbing particles or molecules on the surface of the microresonator, shifting the WGM resonance. In essence we use the microresonator as a nearfield thermometer to measure dissipated heat upon optical excitation. To circumvent the photothermal background of the popular SiO_2 on Si toroidal resonators, we have developed an all-SiO_2 microtoroidal resonator, unlocking visible wavelengths to interrogation. We further employed a double-modulation technique through simultaneous Pound-Drever-Hall locking of the probe beam and amplitude modulation of the pump beam to reach sub-100 Hz or single attometer resonance shift resolution. This corresponds to signals much smaller than that predicted from a single-molecule, and thus represents an avenue toward single-molecule absorption spectroscopy.

We demonstrate this technique by examining gold nanorods (AuNR), which validate our experimental setup with near-diffraction limited photothermal maps, Lorentzian absorption spectra with stochastic center wavelengths, and single dipole polarization dependences. Further, AuNRs in close proximity to microresonator WGMs display signatures of photonic-plasmonic interactions, a forest of Fano resonances decorating the plasmonic absorption feature. This platform offers a facile methodology to study these complex interactions, with thermal annealing of the AuNRs producing highly controllable tuning of Fano resonances. Applying our platform to conductive polymers (CP), we have begun to understand the fundamental properties that enable the high conductivity from a bottom-up nanoscale perspective. We examine the interplay between homogeneous and heterogeneous broadening, measure the long-range ordering, and determine relative surface orientation of CPs. These examples firmly demonstrate the utility of our platform to go beyond sensing allowing exploration of novel characteristics in complex systems and potentially the observation of chemical and biochemical dynamics.

11:00am **NS+AN+EM+MN+MP+RM-TuM10 Optomechanical Interactions for Metrology and Signal Processing*, Karen Grutter,*** The Laboratory for Physical Sciences **INVITED**

Imprinting radio-frequency (RF) signals on optical carriers has a broad range of applications from metrology to communication and has been accomplished in bulk components using a variety of techniques. Achieving this functionality on a chip could broaden the potential application space, but the bulk frequency generation methods do not translate directly to the nanoscale. A number of methods have been proposed for on-chip frequency generation, including various sources of electro-optic modulation, comb generation via material nonlinearities in microresonators, and optomechanical/opto-acoustic interactions. In this talk, we will discuss the features of these sources, with particular focus on optomechanical interactions.

One potential phenomenon enabling opto-acoustic frequency generation is stimulated Brillouin scattering (SBS), which is essentially an interaction between propagating phonons and photons. This effect has been demonstrated in optical fibers, and recent results in on-chip waveguides show promise. One of the challenges with SBS on chip is that gain is dependent on long interaction lengths.

This interaction can be enhanced by moving to a different domain of phonon/photon interaction: cavity optomechanics. In an optomechanical cavity, the characteristics of the generated frequency are dependent on the mechanical eigenmode. We will demonstrate the relationship between mechanical quality factor and phase noise in ring optomechanical oscillators.

The optomechanical interaction can be optimized beyond that of ring resonators by further confining optical and mechanical modes using photonic and phononic crystals. We have designed and fabricated Si_3N_4 nanobeam optomechanical crystals with ~4 GHz mechanical breathing modes. The increased optomechanical coupling of these nanobeams confers high sensitivity to displacement, which could be exploited for various metrology applications, which we will discuss.

Further enhancement of the optomechanical coupling can be achieved by modifying the optomechanical crystal geometry to support an optical slot mode. We have designed and fabricated ~3 GHz-frequency slot-mode optomechanical crystals in Si_3N_4. In addition to increasing the optomechanical coupling compared to the single-nanobeam device, this structure has increased versatility, enabling interaction with other stimuli and modalities. We have integrated NEMS actuators with a slot-mode optomechanical crystal, and used these actuators to tune the optical mode and lock it to an external, fixed laser wavelength. This increases the practicality of this device, enabling longer-term measurements and stabler frequency sources.

11:40am **NS+AN+EM+MN+MP+RM-TuM12 Cold-atom based Sensors and Standards*, Stephen Eckel,*** *D.S. Barker, J.A. Fedchak, N.N. Klimov, E. Norrgard, J. Scherschligt,* National Institute of Standards and Technology **INVITED**

In this talk, I will describe our recent efforts to merge nanophotonics, ultra-high vacuum, and atomic physics together to build a new generation of cold atom sensors and standards. In particular, I will focus on our recent realization of a single-beam system for cooling lithium atoms, an atomic species recently identified as an excellent candidate for a primary vacuum standard. Our system uses a triangular-shaped nanofabricated diffraction grating to produce the necessary beams for a magneto-optical trap that cools and slows the atoms. Unlike systems that use rubidium or cesium, which can be loaded from a vapor, lithium introduces additional complications because it must be produce from a thermal source requiring loading of the magneto-optical trap from behind the chip. Finally, I will conclude by talking about other trap geometries that we are pursuing, how they benefit vacuum and inertial sensors, and what the synergy of integrated nanophotonics, high-vacuum and atomic physics might be able to bring.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room 202A - Session PC+AS+BI+NS+PB+SS-TuM

Solid-Liquid and Gas-Liquid Interfacial Processes and Characterization

Moderators: Stephen Nonnenmann, University of Massachusetts - Amherst, Juan Yao, Pacific Northwest National Laboratory

8:00am **PC+AS+BI+NS+PB+SS-TuM1 Liquefied Gas Electrolytes for Electrochemical Energy Storage Devices***, Y.S. Meng,* University of California San Diego*; **Yangyuchen Yang,*** University of California at San Diego **INVITED**

Electrochemical energy storage devices, such as Li-ion batteries and electrochemical capacitors, have seen little change in their electrolyte chemistry since their commercialization. These liquid electrolytes often limit the energy density and low-temperature operation of these devices, which hinder many potential applications. Our work uses electrolytes based on solvent systems which are typically gaseous under standard conditions and show excellent performance in electrochemical energy storage devices. It has demonstrated that these novel solvents have superior physical and chemical properties which are attributed to excellent performance over an extended temperature range and a wide potential window of stability with unique safety features. The use of fluoromethane as solvent for lithium batteries shows excellent low-temperature operation down to -60 °C with high capacity retention. The liquefied gas electrolytes also show a high coulombic efficiency for cycling dendrite-free lithium metal anodes.

8:40am **PC+AS+BI+NS+PB+SS-TuM3 An *In situ* Molecular-scale View of Nucleation and Self-assembly at Solid-liquid Interfaces***, **James De Yoreo,*** Pacific Northwest National Laboratory **INVITED**

Nucleation and self-assembly from solutions are seminal processes in the formation of ordered structures ranging from simple inorganic crystals to macromolecular matrices. Observations over the past fifteen years have revealed a rich set of hierarchical nucleation pathways involving higher-order species ranging from multi-ion clusters to dense liquid droplets, as well as transient crystalline or amorphous phases. Despite their complexity, a holistic framework for understanding particle-based pathways to crystallization that extends classical concepts emerges when the coupled effects of complexity of free energy landscapes and the impact of dynamical factors that govern particle formation and interaction are considered.Here I use a series of in situ TEM and AFM studies on inorganic, organic, and macromolecular systems to illustrate that framework via the evolution in nucleation and growth processes as these complexities and dynamical factors come into play. The results show that the introduction of either size-dependent phase stability associated with the high surface-to-volume ratios of nanoparticles, or high driving force coupled with the existence of metastable polymorphs leads to two-step pathways characterized by the initial appearance of a bulk precursor phase. The creation of micro-states, which represent local minima in free energy stabilized by configurational factors associated with structural elements of molecules, can also lead to hierarchical pathways, but the intermediates are microscopic transient states that do not appear on a bulk phase diagram. However, small changes in molecular structure can eliminate these transient states, leading to a direct pathway of nucleation.Limitations on molecular mobility, either through large barriers to changes in coordination or conformation, reduced temperature, or introduction of ion-binding polymers, can freeze non-equilibrium states into place for dynamical reasons. Analysis of sub-critical cluster evolution and subsequent nucleation shows that these dynamical constraints can lead to density fluctuations in accordance with classical descriptions even when non-classical pathways dominate.The findings from these in situ studies provide a common basis for understanding the development of order in systems as diverse as simple salt crystals, branched semiconductor nanowires, and microbial membranes.

9:20am **PC+AS+BI+NS+PB+SS-TuM5 Non-linear Surface Spectroscopy at the Aerosol Particle/Gas Interface***, Geiger, **Ariana Gray Be,*** Northwestern University **INVITED**

While the interface of the aerosol gas and particle phase is the first entity encountered by incoming gas phase species, accessing it with bond-specific methods has been hindered due to a lack of tools that can operate under ambient pressure and temperature conditions. Here, we overcome this hurdle by using nonlinear optics and demonstrate the utility of vibrational sum frequency and second harmonic generation for probing the surfaces of sea spray aerosol, secondary organic aerosol, and anthropogenic influence on them. By following the heterogeneous physical and chemical processes that drive gas-to-particle conversion, aerosol formation, their transformations and phase transitions, and reactivity, we provide the molecular origin for cloud activation.

11:00am **PC+AS+BI+NS+PB+SS-TuM10 The Influence of Electrochemical Potential and Water Vapor on Ionic Liquid Binding Energy Shifts Examined by AP-XPS***, **Meng Jia,*** University of Delaware*; A. Broderick, J.T. Newberg,* University of Delaware

Ionic liquids (ILs) have relatively high electrochemical and thermal stability, good conductivity and low volatility, making them inherently “greener and safer” compared to the conventional electrolytes. The application of ILs in the field of electrochemistry has identified many opportunities for their use as electrolytes in electrochemical devices. Due to the ubiquity of water and the hydrophilic nature of ILs, water can either be unintentionally present or often intentionally added to alter IL properties including density, viscosity, friction, and electrochemical window. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) is sensitive to both the chemical and electrical states of materials, which makes it an ideal method for studying surface potentials in electrochemical devices. In this work we examine the IL-gas interface of 1-butyl-3-methylimidazolium acetate, [BMIM][OAc], deposited on an Au foil via AP-XPS as function of electrochemical potential and surrounding water vapor pressure. The electrochemically induced binding energy shifts (ΔBE/ΔE) of carbon, nitrogen, and oxygen species of the IL were analyzed. Results reveal that in the absence of water vapor there is an ohmic drop between the electrode-IL interface and the IL-vacuum interface, giving rise to a ΔBE/ΔE value of less than one. Upon introducing water vapor, forming an IL/water mixture, the ΔBE/ΔE approaches a value of one as a function of increasing pressure. We attribute this behavior to a decrease in the ohmic drop as the IL/water mixture becomes more conductive. These results suggest that the electrochemical potential of the IL-gas interface is influenced by both an external bias and by varying the surrounding relative humidity. The same is likely true for the IL-electrode interface where water is known to be present.

11:20am **PC+AS+BI+NS+PB+SS-TuM11 Role of Air Gas at the Interface between Water and Graphite Surfaces***, **Ing-Shouh Hwang,*** Institute of Physics, Academia Sinica, Taiwan, Republic of China*; C.W. Yang, C.K. Fang,* Institute of Physics, Academia Sinica,Taiwan, Republic of China*; Y.H. Lu,* Institute of Physics, Academia Sinica, Taiwan, Republic of China*; H.C. Ko,* Institute of Physics, Academia Sinica,Taiwan, Republic of China

The saturation concentrations of nitrogen and oxygen in water under ambient conditions are very small (~10 ppm), thus their roles have been largely ignored. Using advanced atomic force microscopy, we study the evolution of gas-containing structures at graphite/water interfaces at room temperature. Our study indicates that gas (mainly nitrogen and oxygen) molecules dissolved in water tend to adsorb onto hydrophobic/water interfaces [1]. In gas-undersaturated water, we observe gradual nucleation and growth of small two-dimensional (2D) ordered domains over time on graphite surfaces [2]. The ordered structures may eventually cover the entire interface. When water is gas-supersaturated or when fresh DI water is briefly heated, we observe cap-shaped fluid nanostructures in addition to the ordered domains [3]. The cap-shaped nanostructures are the so-called interfacial nanobubbles (INBs) or surface nanobubbles, whose nature, stability, and formation remain controversial. When water is slightly gas-supersaturated, we see evolution of the fluid-like structures. The fluid phase first appears as a circular wetting layer ~0.3 nm in thickness and is later transformed into a cap-shaped INB [4]. 2D ordered domains are nucleated and grow over time outside or at the perimeter of the fluid regions, eventually confining growth of the fluid regions to the vertical direction. We determined that INBs and the fluid layers have very similar mechanical properties, suggesting low interfacial tension with water and a liquid-like nature.

Our study suggests that, in gas-undersaturated water, dissolved gas molecules may mainly be in the dispersed monomer form. Their rearrangement with water molecules at hydrophobic/water interface may lead to gradual nucleation and growth of the ordered domains. In gas-supersaturated water, some dissolved gas molecules are well dispersed in water, but others may aggregate into clusters. Adsorption of gas clusters leads to the formation of circular fluid layers at the graphite/water interface. The work clearly shows the crucial role of gas molecules at hydrophobic/water interfaces and has broad implications in diverse research fields.

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11:40am **PC+AS+BI+NS+PB+SS-TuM12 Probing Cluster and Nanoparticle Growth Processes with X-Ray Spectroscopy and Mass Spectrometry***,* ***Musahid Ahmed****, O. Kostko,* Lawrence Berkeley National Laboratory **INVITED**

Tunable synchrotron radiation (VUV and X-rays) provides a universal, yet selective scalpel to decipher molecular information in complex chemical systems when coupled to mass spectrometry and X-Ray spectroscopy. This provides profound insight into molecular growth mechanisms, solvation and electronic structure in clusters, complexes and nanoparticles. In the first part, I will describe how single photon ionization mass spectrometry may be applied to molecular beams to probe molecular growth that is mediated either by ion or neutral pathways. The association and dissociation pathways in acetylene clusters where bonding can change from van der Waals to covalent upon ionization leading to the formation of benzene will be described.[1] I will follow up with very recent results on association of water with “hydrophobic” naphthalene & “hydrophilic” glycerol where subtle non covalent interactions can lead to surprising results in electronic structure and its effect on the hydrogen bonding network of water.

X-ray spectroscopy provides a local probe of a sample’s electronic structure with elemental and site-specificity and is thus ideally suited for probing solvation. Since X-rays can probe surfaces, interfaces and bulk, and more important penetrate matter, it provides for interrogation of buried and confined spaces. Here I will describe a new approach, Velocity Map Imaging X-Ray Photoelectron Spectroscopy coupled to nanoparticle beams[2] that allows for the visualization of dynamic processes in solvation and molecular growth processes. I will describe its’ implementation on aqueous arginine aerosols, where by varying the pH of the constituent solution, evidence is provided that the guanidinium groups are protonated even in a very basic solution (pH 13).[3] A molecular level picture of how charge and proton transport in aqueous solutions of arginine occur emerges by analyzing the energy shifts on the C and N X-ray photoelectron spectra. I will conclude by suggesting new approaches to probe gas liquid interactions and chemistry with X-Ray spectroscopy and microfluidic devices allowing access to liquids in vacuum.[4]

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Plasma Science and Technology Division
Room 104A - Session PS+EM+SE-TuM

Plasma Processing of Challenging Materials - I

Moderators: Necmi Biyikli, University of Connecticut, Jun-Chieh Wang, Applied Materials

8:00am **PS+EM+SE-TuM1 Development and Understanding of Isotropic Etching Process of Si Selectively to Si$_{0.7}$Ge$_{0.3}$***,* ***Sana Rachidi****, A. Campo, V. Loup,* CEA-LETI, France*; N. Posseme,* CEA, LETI, France*; J.M. Hartmann, S. Barnola,* CEA-LETI, France

The vertically stacked wires MOSFET architecture pushes further the scaling limits of the CMOS technology. Now deemed as a possible extension to FinFET, it offers multiple benefits. A low IOFF current is indeed expected, thanks to multi-gate electrostatic control, with a high current drivability due to 3D vertically stacked channels.

The fabrication starts with the epitaxial growth of (Si$_{0.7}$Ge$_{0.3}$/Si) multilayers (8-12 nm for Si and SiGe layers) on blanket SOI substrates. Then, individual and dense arrays of fins were patterned to fabricate stacked-NWs FETs with 40 nm-pitch fins which are 36 nm high and roughly 20 nm wide. After that, dummy gates and spacers are defined prior to the anisotropic etching of the (Si/SiGe) multilayers. Today one of the most critical step in such device realization is the isotropic silicon removal selectively to silicon germanium.

In this study an understanding of selectivity evolution between Si and SiGe as a function of CF4/O2/N2 remote plasma parameters is presented. The experiments performed on 300mm blanket wafers (Si and Si$_{0.7}$Ge$_{0.3}$) have been carried out on CDE-Allegro.

The impact of etching parameters (CF_4, O_2, N_2, microwave-power, pressure and temperature of the electrostatic chuck) and different pre-treatments on etching rates and selectivity is first investigated. X-ray photoelectron spectroscopy (XPS) analyses will show that for Silicon, a SiO_xF_y thick reactive layer is formed on the etched surface and controls its etching regime. As for Si$_{0.7}$Ge$_{0.3}$, a passivation layer of 2 nm is observed. And it contains a mixture of GeO_x and SiO_xF_y species.

Based on these results, application to patterned wafers will be shown. Scanning Electron Microscopy (SEM), Transmission electron microscopy (TEM) and Energy Dispersive X-ray Spectroscopy (EDX or EDS) are here used for the pattern characterisation.

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8:20am **PS+EM+SE-TuM2 III-V/Ge Heterostructure Etching for Through Cell Via Contact Multijunction Solar Cell***,* ***Mathieu de Lafontaine****, G. Gay, C. Petit-Etienne, E. Pargon,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; M. Darnon, A. Jaouad, M. Volatier, S. Fafard, V. Aimez,* 3IT, Univ. de Sherbrooke, Canada

Through cell via contact architecture aims to increase the multijunction solar cell efficiency by 3% and the power yield per wafer by 20% by transferring the front side contact to the backside using insulated and metallized vias. Via hole plasma etching through the III-V/Ge heterostructure is a key step to fabricate this new architecture. It is challenging, as dozens of layers must be anisotropically etched with low roughness and free damage to ensure optimal cell performance. Moreover, etched patterns must have a depth of >30 µm and present >3 aspect ratio. In this abstract, several patterning strategies are presented to address these challenges.

The epiwafers consist of a 8µm-thick III-V heterostructure (InGaP, InGaAs, GaAs, AlInP, AlGaAs, AlGaInP layers and quantum dots) epitaxially grown on Ge substrate. A 5µm thick SiO_2 hard mask (HM) is first deposited by PECVD and patterned by contact photolithography and plasma etching. The optimization of both the lithography and HM opening steps is crucial for an optimal transfer into the III-V/Ge layers. It is observed that sloped and rough hard mask sidewalls after the HM opening step are detrimental to the via hole etching and lead to severe damage on the heterostructure sidewalls. Combining a thick photoresist mask with vertical sidewalls and an optimized $Ar/C_4F_8/O_2$ plasma process developed in a capacitive coupled plasma reactor allows to pattern the 5µm-thick HM with vertical and quite smooth sidewalls.

A room temperature $SiCl_4/Cl_2/H_2$ plasma process was developed in an inductively coupled plasma reactor to etch vias in the III-V/Ge heterostructures. The cell performance loss associated to via etching was almost absent, indicating that such chemistry is suitable for photovoltaic applications. However, some layers present isotropic etching, which is problematic for the via insulation and metallization. Indeed, III-V compounds with low indium concentration are more sensitive to lateral etching, thus creating preferential isotropic etching in several III-V layers. This represents a challenge considering the aspect ratio and the depth targets. Indeed, lateral etching will be even greater for a longer process time. To obtain anisotropic etching, a high temperature (200°C) $SiCl_4/Cl_2/H_2$ process is proposed. The enhanced volatility of the indium by-products combined with the Si-based passivation could improve the anisotropy while maintaining optimal cell performance. FIB-TEM and EDX are performed to characterize both the etch morphology and the passivation layer. Moreover, optoelectrical measurements will assess the cell performance after via etching.

8:40am **PS+EM+SE-TuM3 Feature Scale Modeling of Etching of High Aspect Ratio Silicon Structures in Pulsed Plasmas***, **Wei Tian**, J.-C. Wang, S. Sadighi, J. Kenny, S. Rauf,* Applied Materials

As critical dimensions shrink below 7 nm, etching of high aspect ratio (HAR) Si structures, such as those used for shallow trench isolation (STI), is becoming challenging. Some strategies to deal with these challenges include multi-step cyclic processes and pulsed plasmas. In this paper, we consider a cyclic pulsed plasma process for Si etch. Etching is done by cycling three steps: oxidation (OX), Si main etch (ME) and clean. The OX step passivates the Si sidewalls and protects them during Si ME. Si is mainly etched during the ME step, where the ion energy and angular distribution (IEAD) and ion / neutral flux ratio are controlled through power pulsing. The clean step removes the Cl/Br-containing passivation from the Si surface prior to re-oxidation. Pulsed plasmas have demonstrated several advantages compared to continuous wave (CW) plasmas and have become indispensable in etching of the next generation of microelectronic devices [1-2]. When source power and/or bias power are pulsed, a variety of pulsing modes are possible. Pulsing duty cycles and phase shift provide additional knobs for controlling the etching characteristics. In order to understand the effects of pulsing modes on etching properties, a feature scale model coupled to a plasma model is desired.

In this work, we investigate several pulsing modes during the Si ME step including separate pulsing of the plasma source or bias powers, and their synchronized pulsing. Plasma models for the 3 steps including the pulsed plasma step [3] are coupled to a 3D Monte Carlo feature scale model. Process performance has been quantitatively evaluated by examining etch rates for Si and the SiO_2-like mask, Si/mask etch selectivity, and critical dimensions within the HAR features. When only the radio-frequency (RF) bias power is pulsed, Si and mask etch rates scale with pulse duty cycle. As a result, if Si is etched to the same depth, the HAR trenches are wider at higher duty cycles due to less total oxidation time and less protection of the sidewalls. Source power pulsing provides higher Si etch rate because of RF bias power being on continuously, but suffers from poor mask selectivity. Synchronized pulsing of both the source and RF bias powers in conjunction with phase control provides additional flexibility in modulating the IEAD and the ion/neutral flux ratio. RF bias pulsing and in-phase synchronized pulsing yield the best selectivity for the conditions explored.

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9:00am **PS+EM+SE-TuM4 Plasma Etching of High Aspect Ratio Oxide-Nitride-Oxide Stacks***, S. Huang, C. Hurard,* University of Michigan*; S. Nam, S. Shim, W. Ko,* Samsung Electronics Co., Ltd., Republic of Korea*; **Mark Kushner**,* University of Michigan

Increasing demand for large memory capacity is now being met by 3-dimensional vertical structures. Fabricating these structures requires plasma etching through hundreds of stacked layers resulting in extremely high aspect ratio (up to 100) vias. The stack typically consists of alternately deposited silicon nitride and silicon oxide layers which serve as the sacrificial material and gate dielectric respectively. When combining the high aspect ratio (HAR) and hybrid materials, the etching of oxide-nitride-oxide (ONO) stacks faces both traditional (e.g., aspect ratio dependent etching, bowing and charging) and new challenges (e.g., mixing layers, line edge striation and tapered etch front through several layers).

In this paper, we report on results from a computational investigation of the etching of ONO stacks using tri-frequency capacitively coupled plasmas sustained in fluorocarbon gases. The reactor scale modeling was performed using the Hybrid Plasma Equipment Model (HPEM), from which the neutral and ion fluxes and ion energy and angular distributions (IEADs) to the wafer surface were obtained. The feature scale modeling was performed using the 3-dimensional Monte Carlo Feature Profile Model (MCFPM) with a newly developed polymer mediated fluorocarbon etching mechanism for oxide and nitride.

During the etching of ONO stacks, the etch front quickly evolves to a tapered profile at low aspect ratio (~5) and persists into deeper features, mainly due to re-deposition of sputtered fluorocarbon radicals within the feature. The etch rate generally decreases with increasing aspect ratio due to limited transport of radicals and ions. Conductance, ion reflection from sidewalls and charging all play of role in the flux of reactive species to the etch front. When the etching proceeds through the ONO stack, the etch rate fluctuates, becoming higher for the nitride and lower for the oxide. The formation of scalloping due to different lateral etch rates for each material is observed for some conditions while not for others. The mechanism behind this scalloping, and methods to minimize its effect will be discussed.

* Work supported by Samsung Electronics Co. Ltd, National Science Foundation and the Department of Energy Office of Fusion Energy Sciences.

9:20am **PS+EM+SE-TuM5 Etch Profile Evolution in Poly-silicon using Halogen Containing Plasmas for Next Generation Device Fabrication***, **Shyam Sridhar**, S.A. Voronin, P. Biolsi, A. Ranjan,* TEL Technology Center, America, LLC

The shrinking and introduction of complex three-dimensional device structures poses a great challenge for plasma etching. With ever-decreasing feature pitches, it is extremely important to achieve a near ideal etch profile, i.e. vertical sidewalls and flat etch fronts. The challenges are manifold in etching three-dimensional structures. For example, in etching high aspect ratio square shaped holes, it is difficult to remove the targeted material from the corners, especially at the bottom of the feature.

In this work, we report the impact of process parameters such as ion energy, neutral and ion fluxes on the profile evolution of closely spaced poly Si lines using F, Cl, and Br containing plasmas. Etching in Cl and Br plasmas resulted in anisotropic profiles with bowed and tapered sidewalls. Addition of gases such as oxygen or fluorocarbons to minimize bowing resulted in enhanced tapering of sidewalls. The etch fronts were found to be relatively flat or curved depending on the ion energy. Micro trenching was also found to influence the shape of the etch front. We attempt to extend the learning from etching two-dimensional lines to three-dimensional features, in order to define a better processing space for new and emerging applications.

9:40am **PS+EM+SE-TuM6 Flux and Energy of Reactive Species Arriving at the Etch Front in High Aspect Ratio Features During Plasma Etching of SiO_2 in $Ar/CF_4/CHF_3$ Mixtures***, **Soheila Mohades**,* University of Michigan*; M. Wang, A. Mosden,* TEL Technology Center America, LLC*; M.J. Kushner,* University of Michigan

Multi-frequency, capacitively coupled plasmas (CCPs) provide additional control in semiconductor processing by separating production of ion fluxes from acceleration of ions into the wafer. In dual-frequency capacitively coupled plasmas (DF-CCPs), the higher frequency (HF, tens to hundreds of MHz) sustains the plasma and the lower frequency (LF, a few to 10 MHz) controls acceleration of ions into the wafer. Although the goal is to have completely separate control, changing the frequency and power of the LF does affect the magnitude of reactive fluxes to the wafer in addition to the ion energy and angular distributions (IEADs). As the aspect ratio (AR) of features approaches 100 in high aspect ratio (HAR) etching of dielectrics, the parameter of interest is the flux of reactants that reaches the etch front, which is not necessarily the same as the fluxes that enter the feature. Issues such as side-wall scattering and neutral conductance in the feature modify those fluxes as the AR increases.

In this paper, the IEADs and reactive fluxes reaching the etch front during fluorocarbon plasma etching of SiO_2 were computationally investigated as a function of AR. The feature scale modeling was performed using a 3-dimensional implementation of the Monte Carlo Feature Profile Model (MCFPM). The IEADs and reactive fluxes incident onto the feature were obtained using the 2-dimensional Hybrid Plasma Equipment Model (HPEM). The parameter space for the DF-CCP has LF of a few to 10 MHz, HF of 40 MHz, with powers of 100-1000 W applied to the bottom electrode with and without a dc-augmented top electrode in a gas mixture of $Ar/CF_4/CHF_3$ at 10s of mTorr. The reactive fluxes and energies onto the etch front for AR of up to 100 are discussed for ions, hot-neutrals and thermal neutrals.

* Work supported by TEL Technology Center, America, LLC, National Science Foundation and the Department of Energy Office of Fusion Energy Sciences.

11:00am **PS+EM+SE-TuM10 Wafer-scale Fabrication of Suspended Graphene Nanoribbon Arrays -from Growth Dynamics to Optoelectrical Applications-**, ***Toshiaki Kato***, *T. Kaneko,* Tohoku University, Japan **INVITED**

Graphene nanoribbons (GNRs) combine the unique electronic and spin properties of graphene with a transport gap that arises from quantum confinement and edge effects. This makes them an attractive candidate material for the channels of next-generation transistors. However, the reliable site and alignment control of nanoribbons with high on/off current ratios remains a challenge. We have developed a new, simple, scalable method based on novel plasma catalytic reaction [1-5] for directly fabricating narrow GNRs devices with a clear transport gap [6]. Since the establishment of our novel GNR fabrication method, direct conversion of a Ni nanobar to a suspended GNR is now possible. Indeed, GNRs can be grown at any desired position on an insulating substrate without any post-growth treatment, and the wafer-scale synthesis of suspended GNR arrays with a very high yield (over 98%) is realized [7]. The growth dynamics of suspended GNR is also investigated through the systematic experimental study combined with molecular dynamics simulation and theoretical calculations for phase diagram analysis. The improvement of thermal stability of Ni nanobar can be a key to realize the GNR nucleation in our method, which can be given by supplying higher density of carbon from plasma to liquid-phase Ni nanobar. The wettability of liquid-phase Ni nanobar against to the SiO_2 substrate is also found to be an important factor forming the suspended structure of GNR. It is also revealed that the minimum length of GNR can be decided by the wavelength of Plateau-Rayleigh instability known as a traditional instability of fluid flow. We believe that our results can contribute to pushing the study of atomically thin layered materials from basic science into a new stage related to the optoelectrical applications [8-10] in industrial scale.

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11:40am **PS+EM+SE-TuM12 Investigation of Surface Reactions for GeSbTe-based Phase Change Material: From Etching to Final Sealing Process**, ***Yann Canvel,*** *S. Lagrasta,* STMicroelectronics, France*; C. Boixaderas, S. Barnola,* CEA-LETI, France*; E. Martinez,* CEA/LETI-University Grenoble Alpes, France

Chalcogenide phase-change materials (PCMs), such as Ge-Sb-Te (GST) alloys, have shown outstanding properties, which have led to their successful use for a long time in optical memories (DVDs) and, recently, in non-volatile resistive memories. The latter, known as PCM memories, are among the most promising candidates to be integrated into next generation smart-power and automotive applications [1].

Chalcogenide PCMs exhibit fast and reversible phase transformations between crystalline and amorphous structures with very different resistivity states. This distinctive ability to store the information gives a unique set of features for PCMs, such as fast programming, flexible scalability, high data retention and performing endurance [2][3].

In the perspective of large-scale integration, which means incorporation of the PCM into more and more confined structures, the device performances are getting increasingly more sensitive to surface effects of the GST layer. Thus, it is crucial to maintain a homogeneous stoichiometric composition in the GST surface/volume all along the manufacturing process, particularly during the patterning of PCM cells.

In this study, we examine the main surface reactions that GST material must face and we illustrate how these reactions are likely to modify its composition.

In particular, we will focus on the surface damages generated by different halogen-based plasma etching processes [4][5]. An innovative etching method, compatible with extreme confined structures, will be highlighted.

Then, we will study the oxidation of GST, responsible of the critical surface degradation after the etching process [6]. According to the exposure conditions, the GST surface undergoes some specific chemical modifications that will be pointed out.

Finally, the stability of GST composition will be evaluated at each point of a standard GST patterning process: from etching to final sealing of PCM cells. It will allow us to understand how the chalcogenide material is degraded during the whole process. Some improvements will be exhibited in order to reduce this degradation.

Plasma etching were carried out in a 12 inch planar ICP reactor. And all the surface analyses were performed by using different techniques of material characterization, such as XPS, PP-TOFMS and EDS.

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12:00pm **PS+EM+SE-TuM13 Behaviors of Charged Species in Afterglow of Dual Frequency Pulsed Capacitively Coupled Plasma with a Synchronous Negative DC-bias**, ***Takayoshi Tsutsumi***, *T. Ueyama, K. Ishikawa, H. Kondo, M. Sekine,* Nagoya University, Japan*; Y. Ohya,* Tokyo Electron Miyagi Limited*; M. Hori,* Nagoya University, Japan

Dual frequency pulsed capacitively coupled plasma with a synchronous negative DC-bias to a top electrode is developed for the improvement of high-aspect-ratio contact hole (HARC) fabrications. It enables to suppress the distorted etched profiles such as twisting. These distortions are due to the distortions of ion trajectories inside the deep contact holes, which are charged up positively. It is expected that charged species presented in early afterglow were neutralized on the surfaces in the holes. we focus on the behavior of charged species in the afterglow period of the synchronous negative DC-bias imposition to the top electrode in the pulsed dual frequency CCP.

For temporal change of electron density in the afterglow, the synchronous negative DC-bias resulted in lower decay rate of electron density in afterglow[1]. The result indicate that higher DC-bias imposition causes more electron generation. Moreover, the decay rate near the bottom electrode is lower than that of near the top electrode. The possible explanation is electron generation or sustaining mechanism in the afterglow of DC synchronized pulsed plasma. We measured OES to confirm the electron generation or plasma sustainment in the afterglow. The intensities of Ar emission (at a wavelength of 750.38 nm) in afterglow decreased at the beginning of RF off period and increased after several µs. This phenomenon was not observed in the constant DC-bias condition.

The synchronous DC-bias voltage seems to accelerate the positive ions to the top electrode. And ion bombardment to the top electrode surface enhance the generation of the secondary electron in the afterglow. We consider that this influence the generation of negative ions and the neutralization of the charged surface of the hole in afterglow.

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Plasma Science and Technology Division
Room 104C - Session PS+PB-TuM

Plasma Medicine

Moderator: Deborah O'Connell, University of York, UK

8:00am **PS+PB-TuM1 Lessons from Tesla for Plasma Medicine***, David Graves,* University of California at Berkeley

It can be argued that plasma medicine originated with Nikolai Tesla in the late 19th century when he showed that one could pass large quantities of high frequency currents through a human body with no apparent damage. [1, 2] Tesla interpreted the significant sensations he experienced following exposure to these currents as being potentially valuable therapeutically. Tesla's work inspired much more extensive investigations over a period of several decades by numerous other researchers, on both the physics and biomedical effects of these currents. Researchers such as Arsene d'Arsonval and Paul Oudin in France and Frederick Strong in the United States, among others, were important pioneers. These early pioneers had a surprisingly modern view of some aspects of the therapeutic mechanisms of high frequency currents that clearly overlap with recent results. The perspective of this community was that the most important physiological effects are associated with the high frequency currents rather than the gas phase plasma. Some early work, such as the analgesic effects of dielectric barrier air plasma on tissue, is not well known today. [3] The range of afflictions that early practitioners treated successfully is remarkable. This body of work, in some cases almost 130 years old, has important lessons for current investigations into plasma medicine. Observations from Tesla and other early practitioners suggests that high frequency currents are potentially important and plasma medicine researchers should probably pay more attention to them.

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8:20am **PS+PB-TuM2 Characterization of a Helium Atmospheric Pressure Plasma Jet by Measuring the Total Yield of Reactive Species in Real Time***, **Ek Adhikari**, V. Samara, S. Ptasinska,* University of Notre Dame

Recently, we performed in-situ measurements of reactive oxygen species of a helium atmospheric pressure plasma jet (APPJ) using an acidified ferrous sulfate solution (Fricke) as a sample. The total yield of reactive species reached to or originated in the solution corresponds to the amount of the yield of Fe^{3+} from reactions that transform Fe^{2+} into Fe^{3+} during plasma irradiation. The measurements indicated that the number of reactive species formed in the plasma jet is proportional to the applied pulse voltage and repetition frequency. However, there is a decrease in the yield of Fe^{3+} per pulse for an increase in the frequency. For higher frequencies, there is not enough time to complete all reactions before the next pulse arrives to the sample. Whereas, for lower frequencies, this yield is higher due to the relatively longer time period necessary for reactions to complete. Further, the flow rate of feed gas and treatment distance, which is the distance between the sample and glass capillary, have a minor effect on the formation of reactive species, but the yield of Fe^{3+} gradually decreases for a treatment distance longer than 20 mm. Moreover, we calculated the yield of Fe^{3+} in a very short time (equivalent to time period used in the experiment), and compared with the experimental results. The yield of Fe^{3+} formed within 15 s of plasma irradiation was also compared with the fractions of plasma induced DNA damage level under similar experimental conditions.

8:40am **PS+PB-TuM3 Dry Etching of Patterned Medical Grade Titanium Alloys***, **Eitan Barlaz**, J. Mettler, D.N. Ruzic,* University of Illinois at Urbana-Champaign

We report on the development of a plasma etch process for Ti-6Al-7Nb, an alloy of titanium common for performance biomedical implants due to its excellent mechanical properties and corrosion resistance. The process uses the same chlorine and oxygen chemistry common to etches of pure titanium, with added ion bombardment to remove reaction products with low volatility and to ensure minimal texturing of the surface. The process is capable of etch rates in excess of 50 nm/min in 50 mTorr of Argon and 20 mTorr of CCl_4 using 50 W of RF power and a negative sample bias of > 500 Volts. Due to the need to produce irregularly shaped geometries, relative etch rates are reported for a variety of features including through holes and posts on representative parts. Plasma diagnostics including Langmuir and radical were applied to the process to compare the efficacy of both inductively coupled and surface wave plasma sources over large part sizes.

9:00am **PS+PB-TuM4 Electron Temperature And Plasma Density Of Ar Plasma In Atmospheric Pressure Micro-DBD***, **Pradoong Suanpoot**, J. Sornsakdanuphap,* Maejo University Phrae Campus, Thailand*; B. Ghimire, Y.J. Hong,* Plasma Bioscience Research Center, Republic of Korea*; G. Cho,* Charged Particle Beam and Plasma Laboratory, Republic of Korea*; E.H. Choi,* Plasma Bioscience Research Center, Republic of Korea

A model based on plasma propagation velocity has been recently developed to estimate the electron temperature (T_e) of atmospheric pressure μ-DBD plasma. In this work, we have extended this model to calculate T_e for plasma generated with Ar gas. Plasma has been generated by input discharge voltage of 2.7 kV at driving frequency of ≈ 45 kHz. A high-speed single-frame intensified charged coupled device (ICCD) has been used to observe the space and time-resolved discharge images and estimate the value of plasma propagation velocity (u_g). The value of u_g for Ar plasma has been obtained in the range of 6.2´10^3 m/s. The electron temperature has been calculated for this plasma. The average electron temperature has been found to be about 1.18 eV and the average plasma density has been found to be about 3.62×10^{14} cm^{-3} for Ar plasma. Our results obtained with modified convective-wave packet model can be a new contribution to plasma medicine.

Keywords: Atmospheric-pressure μ-DBD plasma, Ar plasma, plasma propagation speed, electron temperature, plasma density

9:20am **PS+PB-TuM5 Plasma Immunotherapy of Cancers***, **Vandana Miller**, A. Lin, P. Ranieri,* Drexel University*; A. Snook,* Thomas Jefferson University*; A. Fridman,* Drexel University **INVITED**

Non-thermal plasmas are currently being developed as an alternative therapy for cancer. Local application of plasma to tumors *in vivo* has led to reduced tumor size and increased life expectancy of treated animals.[1] The body's immune system plays a vital role in the control of cancer.[3] In fact, cancer immunotherapy, the control of cancer by employing components of the patient's own immune system, is emerging as an appealing strategy.[3] New approaches being explored include increasing the immunogenicity of tumor cells by inducing immunogenic cancer cell death (ICD).[4] ICD of cancerous cells has been demonstrated with certain chemotherapeutic drugs and through physical methods such as X-ray therapy and UVC.[5, 6] Cells undergoing ICD express damage associated molecular patterns (DAMPs) which assist immune responses that may mediate systemic elimination of cancer.[4] We have demonstrated that non-thermal plasma is a good candidate for cancer therapy via immunomodulation by:

direct effects on immune cells[7, 8] and

indirect effects of cancer cell ICD.[8]

The role of plasma augmentation on the immune system, based on our *in vitro* and *in vivo* studies, will be discussed as a potential modality for clinical application in cancers. *In vivo* studies using Balb/c mice inoculated with subcutaneous CT26 colorectal cancer cells, treated with nspDBD plasma showed DAMP signal expression and recruitment of immune cells in the local tumor environment. Furthermore, there was development of a systemic, tumor-specific immune response. This demonstrates that plasma elicits ICD locally, in the treatment area, which leads to beneficial host immune responses both locally and systemically. The clinical potential of plasma cancer immunotherapy will be discussed and the challenges to address will be identified for further development of this technology. Results from a small clinical trial will also be presented.

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11:00am **PS+PB-TuM10 Hydroxyl Radical Footprinting with Plasma-Induced Modification of Biomolecules (PLIMB): A Novel Tool for Protein Structural Analysis***, **Faraz Choudhury**, D.I. Benjamin, B.B. Minkoff, J. Blatz, M.R. Sussman, J.L. Shohet,* University of Wisconsin-Madison

The protein-therapeutic industry, typified by anti-cancer proteins like Herceptin, has accelerated the need to be able to analyze the 3-dimensional structure of proteins in solution. Mass spectrometry is widely used for this. This has generated a need for new types of probes that covalently label protein solvent-accessible sites. Two common ones rely upon the creation of and covalent modification with highly reactive hydroxyl (OH) radicals. The first, fast photochemical oxidation of proteins (FPOP), generates hydroxyls from H_2O_2 via laser photolysis, and the second, synchrotron X-ray beam exposure, produces OH radicals via direct radiolysis of water. These techniques suffer from issues such as: a reaction times that are potentially too long to correctly measure protein structure or the necessity to add chemicals. Furthermore, both are cumbersome & expensive, either by accessing a synchrotron or building an instrument to perform FPOP. As a result of a collaboration at the interface of plasma physics and biochemistry, we developed a technique that generates µsecond bursts of OH radicals, using a surface-barrier discharge, for labeling proteins at solvent-accessible amino acid side chains. We call this Plasma-Induced Modification of Biomolecules (PLIMB). PLIMB does not require chemical additives, circumvents the issues associated with reaction timescale, and ultimately costs far less. Using a model protein in solution, cytochrome C, the protein was modified in a dose-dependent fashion in only a lightly buffered water-based solution, demonstrating that the system can generate OH radicals capable of labeling proteins without additional reagents. In addition, only discrete peptides within the protein are modified. Perturbing protein structure via digestion prior to plasma exposure significantly increases the observed covalent modification, suggesting that conformational structure is maintained during exposure. Experiments with myoglobin, a second protein, also revealed distinct regions of modification despite examining in depth the entirety of the protein's sequence. Mapping the oxidized peptides to myoglobin's crystal structure reveals that all of these peptides fall within the same face of the protein, suggesting the preservation of a higher-order structure under the solution conditions described. These experiments suggest that PLIMB provides a means of efficaciously generating microsecond bursts of OH radicals while providing a low cost and readily accessible means of probing the conformation of proteins in solution using mass spectrometry. We envision PLIMB being useful in a wide range of biological, medical and pharmaceutical fields.

11:20am **PS+PB-TuM11 Biological Effects of Plasma-Irradiated Organic Molecules in Plasma- Treated Liquids***, **Kenji Ishikawa**, Y. Hosoi, D. Kanno, Y. Kurokawa, H. Tanaka, M. Mizuno, F. Kikkawa, M. Hori,* Nagoya University, Japan

Selective killing of cancer cells incubated in non-equilibrium atmospheric pressure plasma (NEAPP)-activated medium (PAM) has been reported.[1] This antitumor effect revealed by involvement of reactive oxygen and nitrogen species (RONS) in PAM.[2] The effect was also found in plasma-activated lactate in Ringer's solution (Lactec), so called as PAL.[3] We found that the cancer cells incubated in the PAL received lesser oxidative stress than that of the PAM.[3] A cause of intracellular oxidation with respect to the RONS reactions has been studied by nuclear magnetic resonance (NMR) analysis of organic substances in the Lactec solution.

From the NMR measurements, reactive organic acids, that is, plasma activated lactate (LA) involved pyruvic acid (PA) and acetic acid (AA)-like components in the PAL were detected. The plasma activated organic acids act potentially as antitumor agents other than RONS.

Furthermore, NEAPPs irradiated to fullerenol. The plasma irradiated fullerenol demonstrated a cytotoxic effect on cells. The PF was modified by the plasma irradiation, arising carbonyl groups, ether bonds, and intercalated nitrate anion. Endocytosis of the PF induced to apoptotic cell death and generated intracellular RONS on cells cultured in the PF-added cell culture medium.

1 mL of fullerenol-added water (1.6 mM) was irradiated by the NEAPP (Ar 2 slm) for 3 min. Precipitates of the PF were collected by drying water at 70°C for 1 hr. The collected PF dissolved again into 50 µM of cell culture media (DMEM). 5×10^3 of HeLa cells were cultured for 24 hr in the PF-added DMEM and the same amount (50 µM) of fullerenol-added DMEM, respectively. Cell viability was evaluated by the MTS assay. Caspase activation and fullerenol permeation of the cell membrane were observed by fluorescent microscopy.

Although the viability of the fullerenol-added DMEM remained at a constant of 110 %, the HeLa cell viability decreased to 70 %, when the cells were incubated in the PF-added DMEM. The cells showed caspase 3/7 activation. The PF activate the caspase cascade pathway to induce apoptosis and permeation of the fullerenol into the cells. Therefore, the fullerenol properties were modified by the plasma-irradiation to enhance the cytotoxicity of PF.

Acknowledgments This study was supported by KAKENHI 24108002.

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11:40am **PS+PB-TuM12 OH-Radical Generation in an Atmospheric-Pressure Plasma Discharge for use in Three-Dimensional Protein Structural Analysis***, **Joshua Blatz**, B.B. Minkoff, F.A. Choudhury, D.I. Benjamin, J.L. Shohet, M.R. Sussman,* University of Wisconsin-Madison

Atmospheric-pressure plasma discharges are well-known to generate OH radicals when interacting with water. However, the use of radicals created in this way for protein footprinting is virtually non-existent. Here, we describe a novel technique which utilizes a dielectric-barrier plasma discharge to oxidize proteins in solution. These oxidation events are quantified using mass spectrometry and allows us to determine the exterior domain and solvent accessibility of a protein.

To generate the plasma a high-voltage A.C. signal is applied to a needle electrode in close proximity to the surface of the liquid sample. This causes the gas to breakdown and form the plasma. These plasma discharges have been measured to be on the order of microseconds which prevents the protein from cleaving. During plasma exposure the sample is cooled to maintain temperature and prevent denaturation.

Protein bovine serum albumin was exposed to plasma. Labeling of the exterior domain was found in a manner consistent with other protein structural analysis techniques. Additionally, initial measurements have been collected which indicate that by changing various electrical, physical, and chemical parameters the technique may still be optimized. This could lead to greater OH-radical generation, reduced sample heating, and reduced pH change.

In addition to the consistent initial results and optimization potential there are many advantages it holds over competing techniques. It can be built inexpensively and on a space-limited benchtop. There are no necessary chemical additives which may interfere with the results and there seems to be no limit to the size of the protein which can be treated. All the samples are treated in liquid solution so they are free to move as they would *in vivo*.

12:00pm **PS+PB-TuM13 Plasma-Surface Interaction at Atmospheric Pressure: From Mechanisms with Model Polymers to Applications for Sterilization***, **Pingshan Luan**[1], G.S. Oehrlein,* University of Maryland, College Park

Cold atmospheric plasma (CAP) produces many types of chemically reactive species and is capable of modifying materials at atmospheric pressure. Studying plasma-surface interaction (PSI) at such pressure has been challenging due to the small mean-free-path (< 100 nm) which prohibits the method of using independently controlled beams of ions/neutrals. In the past few years, we developed an alternative approach of studying PSI at atmospheric pressure using well-controlled source-ambient-sample systems and comprehensive characterization techniques. First, we characterized and compared a few types of CAP sources such as atmospheric pressure plasma jet (APPJ) and surface micro-discharge (SMD). We found that the dominant reactive species generated by different CAP sources can be dramatically different. By tuning source operating parameters, we were able to manipulate the dominant reactants generated by these sources. Second, by controlling the gaseous environment wherein PSI took place, we could suppress certain unwanted interactions of plasma species with the ambient and regulate the delivery of reactive species to material surfaces. Lastly, we used polymers with representative functional groups to study the effect of reactive species on certain surface moieties. Due to the multi-phase nature of PSI, we integrated many characterization techniques in our study, including that of plasma/gas phases such as optical emission spectroscopy (OES), Fourier transform infrared spectroscopy (FTIR) and UV absorption, and that of

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

material surfaces such as X-ray photoelectron spectroscopy (XPS), attenuated total reflection (ATR) FTIR and Ellipsometry. To our knowledge, the perpendicular electric field enhanced ATR-FTIR was used for the first time to study plasma processed polymer films less than 10 nm-thick. Combined with XPS, these techniques provide rich chemical information of both surface and subsurface modifications. By correlating plasma/gas phase with surface/subsurface measurements, we showed the dominant effect of a few types of reactive species such as O, OH and N_2O_5 on materials. We also provided evidence showing the competition between etching and surface modification during plasma treatment. Besides, we extended our investigation to studying the CAP-induced bacterial membrane damage, which might help understand the sterilization mechanism of CAP. We gratefully acknowledge funding from National Science Foundation (PHY-1415353) and US Department of Energy (DE-SC0001939). We thank Andrew J. Knoll, Elliot A. J. Bartis, V. S. S. K. Kondeti, Peter J. Bruggeman, Andrea Gilbert, Rohan Tikekar and David B. Graves for collaborations.

Advanced Surface Engineering Division
Room 202C - Session SE+PS-TuM

Plasma-assisted Surface Modification and Deposition Processes

Moderators: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Matjaz Panjan, Jozef Stefan Institute, Slovenia

8:00am **SE+PS-TuM1 Surface Modification of 304 Stainless Steel by Neutral Nitriding*, Petros Abraha,*** Meijo University, Japan

Austenitic stainless steel is the choice of material in the manufacturing industries for its corrosion resistance but lacks surface hardness leading to poor wear resistance and ultimately short lifetime. Stainless steel possesses the same microstructure at all temperatures and therefore, cannot be hardened by heat treatment. Attempts to increase the hardness of austenitic stainless steels by plasma nitriding has been successfully demonstrated in using different processes and methods. Here, we have introduced a nitriding method that improves the hardness and corrosion resistance of stainless steel while maintaining the initial surface conditions of the untreated surface.

In this research, neutral nitriding, a plasma nitriding method performed on a sample inside a cathodic grid in using an electron beam excited plasma device is presented. In this method, nitrogen ion incidence onto the sample surface is prevented by a positive bias to the sample ultimately controlling the formation of the compound layer. Further, the incidence of electrons causing an excessive rise in sample temperature is prevented by applying a negative bias to the cathodic grid. The setup creates a favorable condition that enables the neutral nitrogen species to be the primary species within the plasma to diffuse into the sub-surface of the sample and form a hardened layer.

The results obtained are as follows: (1) The S-phase without any compound layer on the surface was confirmed and the surface roughness of the untreated surface (Ra 10 nm) was maintained (Ra 15 nm). (2) The surface hardness was increased to more than two times, 550 Hv. (3) Pitting potential tests confirm Improved critical pitting potential on samples nitrided at 350 °C and 375 °C.

8:20am **SE+PS-TuM2 Plasma Cratering and Hardening for Friction Reduction and Wear Resistance of Cast Iron*, Wei Zha,*** Univesity of Windsor, Canada*; C. Zhao, X. Nie,* University of Windsor, Canada

Cathodic plasma electrolysis (CPE) is used to reduce the friction and increase the wear resistance of cast iron. During the process, cast iron sample serves as a cathode where the plasma discharging occurs, increasing the surface hardness and leaving an irregular array of craters on the surface. As the applied voltage increases, the number and size of craters become larger. The areal density of craters (as reservoir) and oil retention are determined from SEM image analysis and surface profiler. Reciprocating tribotests are conducted on blank sample, CPE-treated samples and sample with crosshatched surface. The results show that the CPE-treated samples can have a lower coefficient of friction and higher wear resistance than other two kinds of samples. As for the CPE-treated samples, the friction behaviors are also discussed by considering effects from their areal density of craters, surface roughness and oil retention.

Keywords: Cathodic plasma electrolysis, Cratering, Hardening, Friction, Wear

8:40am **SE+PS-TuM3 Area-selective Deposition by Surface Engineering for Applications in Nanoelectronics. From Blanket to Confined Dimensions*, Silvia Armini,*** IMEC, Belgium

At advanced nodes targeting 10nm feature size and below, lithography starts to dominate costs (EUV, multiple mask passes per layer, pattern placement error). Complementary techniques and materials are needed to continue 2D scaling and extend the Moore's law. Area-selective atomic layer deposition (AS-ALD) is rapidly gaining interest because of its potential application in self-aligned fabrication schemes for next-generation nanoelectronics. The strong sensitivity of ALD to the chemistry of the surface and its self-limiting nature are particularly appealing. In this talk we report two examples of AS deposition triggered by i) area activation, i.e. a H2-based plasma triggered selective placement of ALD Ru catalyst on SiCN liner with respect to amorphous carbon materials (Fig. 1) followed by AS electroless metal bottom-up deposition and ii) area deactivation by a combination of surface functionalization by molecular self-assembled organic films and ALD of metal oxides and metal nitrides. In the latter case the idea is to chemically and locally bond a molecule directly to the metal surface in order to inhibit reactive sites and then prevent further reactions between the precursor molecules and the surface. A selectivity driven benchmarking of organic passivation films deposited on copper surface from the vapor and liquid phase will be presented, both on blanket surfaces, micron-scale and nanometer-scale patterned features. Two major challanges will be investigated: i) defectivity induced by a reactive ALD process which also nucleates on the part of the surface covered with the organics and metrology; ii) understanding and control of AS ALD material shape at the boundaries between Cu and dielectrics. In Fig.2 the top-down SEM images after AS ALD Hf nitride on 240nm Si oxide/50nm Cu lines are shown. A target thickness of 10nm Hf nitride is deposited by ALD at 120˚C.

9:00am **SE+PS-TuM4 Experimental and Numerical Evaluation of Cohesive and Adhesive Failure Modes during Indentation of TiAlN Coatings on Si(100) Deposited by MPPMS*, Z.T. Jiang,*** *M.K. Lei,* Dalian University of Technology, China

The mechanical behavior of TiAlN coatings was studied by Indentation test and FEM modeling. The TiAlN coatings were deposited by modulated pulse power (MPP) magnetron sputtering. The peak power was used from 21 kW to 50 kW with the gas flow ratio of $Ar/N_2=4:1$. The microstructure of the indented regions was observed by focused ion beam (FIB), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD with grazing angle of incidence reveals that the coatings consisted with c-TiAlN. The achieved hardness and modulus for the coatings show significant increase from 23.6 GPa to 46.7 GPa and 396 GPa to 461 GPa. The eXtended Finite Element Method (XFEM) was applied to study the cohesive cracks through the coatings, while the Cohesive Zone Model (CZM) was to evaluate the coating/substrate interfacial crack. The stress transfer from the coating to the substrate was dependent on the elastic and elastic/plastic properties of the coating and substrate. The energy release rate of the coating and the cohesive zone parameters were investigated by the fracture toughness of the coatings. Compared with the experimental results, the simulation results were able to accurately observe the deformation as well as the fracture behavior of the coatings. Under indentation loading, the crack initiation tended to begin at the outer surface and to propagate along the coating in thickness direction until the cracks reached the substrate.

9:20am **SE+PS-TuM5 Growth of TiB_x Thin Films by DC Magnetron Sputtering and High-Power Impulse Magnetron Sputtering: Effect of Pressure and Substrate Temperature*, Niklas Hellgren,*** Messiah College*; J. Thörnberg, I. Zhirkov,* Linköping University, Sweden*; G. Greczynski,* Linköping University, Sweden*; J.P. Palisaitis,* Linköping University, Sweden*; M. Sortica,* Uppsala University, Sweden*; P.O.A. Persson,* Linköping University, Sweden*; I. Petrov, J.E. Greene,* University of Illinois at Urbana-Champaign*; L. Hultman, J. Rosen,* Linköping University, Sweden

We report on titanium boride, TiB_x, thin films grown by both direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS) from a compound TiB_2 target, in an attempt to grow high-quality stoichiometric TiB_2 films. The composition, microstructure, and texture was analyzed as a function of deposition temperature (room temperature – 900 °C) and pressure (5 – 20 mTorr). Films deposited by DCMS at low pressure, regardless of temperature, result in over-stoichiometric films (B/Ti ≈ 3), while high pressure gives close to stoichiometric films. This can be explained by differences in angular distribution of sputtered B and Ti atoms, as well as differences in gas scattering [1]. These high-pressure films, however, are under-dense and have a mixed 100/101 preferred crystal orientation.

The composition of the HiPIMS-deposited films show a more complex dependence on pressure and temperature: At low temperatures, the trend vs pressure is opposite to DCMS, with the higher pressure resulting in higher B/Ti ratio. At higher temperatures, the effect of pressure is smaller, and even reverses slightly, with higher pressure giving lower B/Ti ratio.

We attribute these trends to a combination of several factors: (1) The much higher degree of ionization in HiPIMS, and the different transport of the ionized sputtered particles in the presence of a magnetic field, (2) gas density decrease at higher temperature resulting in less scattering, and (3) more sublimation, primarily of boron, at higher substrate temperatures. The highest quality stoichiometric TiB_2 films, with 001-textured nano-columnar structure, form by HiPIMS at 5 mTorr and 500-700 °C.

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9:40am **SE+PS-TuM6 Time-resolved Analysis of the Cathodic Arc Plasma from Nb-Al Cathodes***, S. Zöhrer,* Montanuniversität Leoben, Austria*; A. Anders,* Lawrence Berkeley National Laboratory, Leibniz Institute of Surface Engineering (IOM), Leipzig, Germany*; D. Holec, **Robert Franz,*** Montanuniversität Leoben, Austria

Cathodic arc deposition has been established as one of the standard techniques for the physical vapour deposition of thin films and coatings as it allows the synthesis of a wide variety of materials including metallic films, but also nitrides, carbides and oxides if a reactive background gas is used. In addition, the highly ionised plasma and the achievable high deposition rates allow a variety of control mechanisms to influence the film growth while the manufacturing costs remain rather low due to the short deposition times. With the advent of multifunctional thin films and coatings, the use of multi-element cathodes providing the non-gaseous elements during the synthesis has become an industrial standard. However, a detailed understanding of the discharge properties is vital for the further optimisation of the deposition processes to enable synthesising thin films or coatings with improved properties.

By using a time-resolved method in combination with pulsed arcs and a comprehensive Nb-Al cathode model system in this work, we investigate the influence of cathode composition on the plasma, while making the influence of neutrals visible for the observed time frame. This model system consists out of three different Nb-Al compositions with the atomic ratios 75/25, 67/33 and 25/75, as well as pure Nb and Al cathodes. The results visualize ion detections of 600 µs plasma pulses, extracted 0.27 m from the cathode, resolved in mass-per-charge, energy-per-charge and time. In addition to high vacuum at a base pressure of 10^{-4} Pa, the measurements were carried out at three elevated Ar gas pressures: 0.04 Pa, 0.20 Pa and 0.40 Pa. Ion properties were generally found to be strongly dependent on the cathode material in a way that cannot be deduced by simple linear extrapolation. For high vacuum, current hypotheses in cathodic vacuum arc physics applying to multielement cathodes, like the so called “velocity rule” or the “cohesive energy rule”, are tested for early and late stages of the pulse. In addition, the influence of an inert background gas is analysed by comparing the results with those at increased pressure, which show reduced ion charge states, up to a state where mostly Nb^{2+} and Al^{1+} ions are detected. Beside Nb and Al ions, time-resolved energy and charge distributions of Ar ions are taken into account, providing further insights on the processes involved.

11:00am **SE+PS-TuM10 Dedicated Experiments to Challenge a Model for Reactive Magnetron Sputtering***, **Diederik Depla,*** Ghent University, Belgium **INVITED**

Reactive magnetron sputter deposition is conceptual easy technique which can be explained in a few lines. Behind this apparent simplicity there is a complex interplay between different plasma and surface related processes. To get a better understanding of the impact of the different process parameters, modelling is inevitable. Therefore, the paper will first focus on the RSD (Reactive Sputter Deposition) model. As this code is freely downloadable and it has a GUI, it permits not only the research team to investigate this fascinating deposition technique, but also you. Important target processes such as sputtering, chemisorption, direct and knock-on reactive ion implantation will be discussed. With the model as a guide, some important fundamental questions will be tackled. Experiments related to the transition from metallic to poisoned mode, the deposition rate during reactive sputtering, the presence of parameter hysteresis will be presented. The confrontation between model and experiment will highlight not only the success of the RSD model, but also the further challenges to improve this model, and our understanding of reactive magnetron sputtering.

11:40am **SE+PS-TuM12 Current-voltage-time Characteristics of HiPIMS Discharges Revisited***, **André Anders,*** Leibniz Institute of Surface Engineering (IOM), Germany

Continuous discharges can be characterized by their current-voltage (*I-V*) characteristics, which expresses the quasi-steady-state plasma impedance for slowly varying parameters of the driving circuit. For fast and strongly changing conditions, the plasma impedance may become a strong function of time and therefore one needs to explicitly add time as a parameter, leading to current-voltage-time (*I-V-t*) characteristics .

This general approach is applicable to magnetron sputtering, where the magnetron’s *I-V* characteristic is a power law, $I = K V^n$, with K being a device-specific constant and the power exponent n typically in the range from 6 to 10. For HiPIMS, the current is a strong function of time, and one needs to consider *I-V-t* characteristics [1]. In the special case when HiPIMS pulses have similar pulse shapes $I(t)$ at various voltages, one may reduce the description to *peak* current - voltage characteristics and arrive again at a power law $I_p = K V^n$, this time with n in the range between 1 and 2. Most interesting, however, is the case when the $I(t)$ curves are more complicated because they contain additional information. Since the appearance of publication [1] more than a decade ago we have learned a lot about HiPIMS, such as the relative importance of self-sputtering and gas recycling [2], leading to a more unified model [3]. In this contribution, *I-V-t* characteristics are revisited in light of today’s knowledge.

Acknowledgments: The experimental data for this work were primarily generated during the tenure of the author at Lawrence Berkeley National Laboratory, Berkeley, California.

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12:00pm **SE+PS-TuM13 Advantages Associated with Applying a Positive Pulse Option to a HIPIMS Power Supply***, **Jason Hrebik,*** Kurt J. Lesker Company

HIPIMS is an ionized PVC technique that produces a high density, high performance films. The extreme power densities in HIPIMS create a higher ionized plasma that creates a very high energy of material being deposited onto the substrate.

Many advanced techniques have been found to further enhance the quality of HIPIMS films, creating more ideal process and applications for utilizing this technique.

We will show advantages of integrating a positive “kick” pulse into a HIPIMS application. The “kick” pulse is an ideal feature for reactive sputtering applications due to its ability to carry out the HIPIMS plasma for extended period of time, minimizing the disapperating anode effect and repelling metal ions from the plasma toward the substrate resulting in higher sputtering rates.

Surface Science Division
Room 203C - Session SS+HC+NS+PS-TuM

Controlling Mechanisms of Surface Chemical Reactions

Moderators: Bruce D. Kay, Pacific Northwest National Laboratory, Arthur Utz, Tufts University

8:40am **SS+HC+NS+PS-TuM3 Stability and Reactivity of Isolated Rh_1 Atoms on Fe_3O_4(001)***, **Gareth Parkinson,*** TU Wien, Austria

In this talk I will address the thermal and chemical stability of Rh adatoms adsorbed on Fe_3O_4(001), and discuss the reactivity of these species with a view to single-atom catalysis. Using a combination of atomic-scale imaging, spectroscopies and DFT-based calculations, I will show that Rh adatoms adsorb in a bulk-continuation cation site at room temperature on Fe_3O_4(001), where they remain stable upon CO adsorption and can catalyze CO oxidation via a reaction with the support at 500 K. However, at this temperature Rh begins to incorporate within the support lattice, and the higher coordination environment significantly modifies the reactivity. In addition, I will show that Rh1 species efficiently dissociate water, leading to H spillover of H onto the support, and that Rh1 diffusion is induced upon adsorption of O_2 and NO.

9:00am **SS+HC+NS+PS-TuM4 The Mechanism of Glaser Coupling Reactions on Ag(111) and Cu(111) Surfaces: a Case for Halogen Substituted Terminal Alkyne***, T. Wang, H.F. Lv, L. Feng, J.M. Huang, X.J. Wu,* University of Science and Technology of China*; **Junfa Zhu,*** National Synchrotron Radiation Laboratory and Department of Chemical Physics, University of Science and Technology of China

Ullman and Glaser homo-couplings are the two most well-developed on-surface coupling reactions, which have been successfully employed to fabricate one-dimensional and two-dimensional nanostructures on metal surfaces. The mechanism towards surface-confined Ullman coupling has been well-established. However, the mechanism of surface-confined Glaser coupling has been poorly understood. In this presentation, we report our recent studies on the surface-confined Glaser coupling reactions on Ag(111) and Cu(111) using 1,1′-biphenyl,4-bromo-4′-ethynyl (BPBE) as the precursor molecule. By direct observations of alkynyl-Ag-alkynyl and alkynyl-Cu-alkynyl type organometallic intermediates on Ag(111) and Cu(111), respectively, we have proposed a reaction pathway initiated by single-molecule dehydrogenation, similar as the mechanism of on-surface Ullman coupling. The reaction processes were further explored by density functional theory based transition state calculations. Interestingly, the dehydrogenation of terminal alkyne is revealed as a H adatom-related process on Ag(111) while a Cu adatom-related process on Cu(111). After the release of interstitial metal adatoms in the organometallic intermediates, the final C-C coupling occurs easily on Ag(111), but shows extremely low efficiency on Cu(111) due to the too strong interaction between ethynylene and the Cu(111) substrate. In addition, we have demonstrated that Glaser reaction of the molecule is prior to Ullman reaction on Ag(111), which provides a promising approach of stepwise fabrication of sp-hybrid nanostructures. *This work is supported by the National Natural Science Foundation of China (21773222, 21473178) and the National Key R&D Program of China (2017YFA0403402).*

9:20am **SS+HC+NS+PS-TuM5 The Step Sites of Ultrathin ZnO Promote Methanol Oxidation to Formaldehyde***, **Xingyi Deng**, D.C. Sorescu, J. Lee,* National Energy Technology Laboratory

We investigated the adsorption and oxidation of methanol on ultrathin ZnO layers supported on Au(111) using temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) calculations. In the TPRS experiments, we found that only molecular methanol-^{18}O desorbed from the planar ZnO bilayer surface at T = 220 K and 260 K following adsorption of methanol-^{18}O at T = 100 K, whereas a partial oxidation product, formaldehyde-^{18}O (~95% selectivity), and a small amount of carbon dioxide ($C^{16}O^{18}O$) were produced at T = 580 K at the bilayer-trilayer step sites. Computational modeling based on the DFT calculations identified the adsorption configurations of methanol on the planar ZnO surface and at the step sites, as well as the reaction pathways to gaseous formaldehyde. The most stable adsorption configuration was found to be a methanol molecule adsorbed at the bilayer-trilayer step sites with its C-O axis parallel to the upper terrace edge, forming a bond between its O atom and a Zn site on the lower terrace, and also a hydrogen bond between its H atom in the OH group and a lattice O anion at the upper terrace edge. Starting from the most stable adsorption configuration at the step sites, formation of gaseous formaldehyde was shown to take place preferentially via a methoxy (CH_3O(ad)) intermediate, following the pathways CH_3OH(ad) → CH_3O(ad) + H(ad) → CH_2O(g) + 2H(ad) with an overall barrier of 19.0 kcal/mol. Formation of CO_2 was kinetically hindered due to a much larger barrier of ~ 38 kcal/mol to produce a lattice O-bonded formaldehyde ($H_2COO_{lattice}$(ad)), the proposed precursor leading to CO_2. These computational results suggesting the preference to produce gaseous formaldehyde from methanol oxidation at the step sites agreed well with the high selectivity toward formaldehyde observed in the TPRS experiments.

11:00am **SS+HC+NS+PS-TuM10 Investigation of Configuration Change in Water Clusters on a Bilayer ZnO Surface***, **Junseok Lee**, D.C. Sorescu, X. Deng,* National Energy Technology Laboratory

Adsorption of water on the nanostructured metal oxide surfaces has implications in catalysis and serves as a prototypical system in studying water-oxide interfaces. In many cases, the water molecules form hydrogen bonded clusters or extended networks on surfaces. On a bilayer ZnO/Au(111) surface, two types of cyclic triangular water clusters are found to be formed at a specific Moire domain. By using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, the behavior of the water clusters on the bilayer ZnO surface have been further interrogated. The configurations of the two types of cyclic water clusters can be converted to each other by the excitation from the STM tip at a threshold energy. In addition, another pathway for the cluster configuration change was identified at a higher electron energy where the cyclic water clusters could be turned into non-cyclic clusters reversibly. The physical origin of the configuration changes will be discussed.

11:20am **SS+HC+NS+PS-TuM11 Oxygen Reduction Reaction on Fullerene***, **Yosuke Kikuchi**, J.N. Nakamura,* The University of Electro-Communications (UEC-Tokyo), Japan

It has been reported that nitrogen-doped graphene exhibits high oxygen reduction reaction (ORR) activity, while pristine graphene does not [1]. This is because that doped-nitrogen atoms provide extra electrons to graphene, leading to the stabilization of the reaction intermediates on graphene surface. On the other hand, if curvature can be given to graphene, the chemical bond nature between carbon atoms varies from pure sp^2 to sp^3-like sp^2, and then the reactivity of graphene surface is expected to increase. In this study, we evaluated the ORR activity of fullerene as an example of carbon materials with a curvature.

We investigated the ORR activity of fullerene (C_{60}) using first-principles calculations based on the density functional theory. Electrocatalytic activities were evaluated on the basis of the computational hydrogen electrode model proposed by Nørskov *et al*. [3] We evaluated the energetics of reaction intermediates in terms of free energy of adsorption. In general, the ORR mainly proceeds in two pathways: For the two-electron pathway ($2e^-$), oxygen molecule (O_2) is reduced to hydrogen peroxide (H_2O_2), and for the direct four-electron pathway ($4e^-$), the final product is water (H_2O). H_2O_2 for the $2e^-$ pathway might corrode a carbon-based electrocatalyst material itself, causing to low durability. Therefore, we also played up the selectivity for the $4e^-$ pathway.

It was found that the fullerene molecule has ORR activity with extremely high selectivity for the four-electron pathway, even if the nitrogen atom is not doped. On the other hand, nitrogen-doped fullerene hardly shows the ORR activity, because the reaction intermediates are overstabilized by nitrogen-doping to fullerene; the maximum electrode potentials show negative values for both the direct four-electron and two-electron pathways.

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[2] S. Ni, Z. Li, J. Yang, Nanoscale, 4, 1184 (2012)

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11:40am **SS+HC+NS+PS-TuM12 Surface Structure and Reactivity of Ni-Cu Single-Atom Alloys***, **Dipna Patel**, E.C.H. Sykes,* Tufts University

Ni is one of the most extensively used industrial catalytic metals. Utilized for steam reforming of hydrocarbons, Ni atom ensembles detrimentally catalyze the formation of graphitic carbon which leads to coking and deactivation of the catalyst. By alloying Ni into Cu, a catalytically less active host metal, our single-atom alloy approach has the potential to greatly enhance catalytic selectivity and reduce poisoning, analogous to other systems such as Pt-Cu and Pd-Cu. First, we report characterization of the atomic-scale surface structure and local geometry of low coverages of Ni deposited on a Cu(111) single crystal, using scanning tunneling microscopy. Near room temperature, Ni preferentially alloys into the Cu host by forming Ni rich brims along ascending step edges. Next, temperature programmed desorption studies reveal that CO binds more weakly to single Ni atoms in Cu compared to larger Ni ensembles in Ni(111) which is promising for catalytic applications in which CO poisoning is an issue. This characterization of Ni-Cu surface alloys the catalytic activity and selectivity of the surface to be correlated with the atomic-scale structure of the alloy. Using this approach, the catalytic selectivity and resilience to poisoning can be tuned via both ligand and ensemble effects.

12:00pm **SS+HC+NS+PS-TuM13 Effective Local Structure for Bottom-up Designed ORR Catalyst Using Pyridinic Nitrogen Containing Molecules***, **Kotarou Takeyasu**, Y. Shimoyama, M. Furukawa, S. Singh, J. Nakamura,* University of Tsukuba, Japan

Nitrogen containing carbon materials have been reported to be low-cost and durable catalysts for reactions such as an oxygen reduction reaction ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) was found to create ORR active sites in our previous work [1]. Recently, we also have shown that the active site is superseded by pyridinic nitrogen-containing aromatic molecules covering a carbon substrate with high density [2]. That is, bottom-up catalysts composed of pyridinic nitrogen-containing molecules and carbon supports. In the present study, we aim to investigate which local structure for pyridinic nitrogen in a molecule strongly contributes to the ORR activities and to clarify the mechanism.

For this purpose, various nitrogen-containing molecules were prepared, which were 1,10-phenanthroline, 4,7-phenanthroline, 1,7-phenanthroline, benzo[h]quinoline, phenanthridine, acridine, phenazine, quinoxaline, and dipyridophenazine. The bottom-up catalysts were prepared by simply immersing carbon black (CB) as a support material into a catalyst solution with solvent of nafion. The catalytic performances for oxygen reduction reactions (ORR) of the prepared catalysts were measured by rotating disc method in acidic electrolyte (0.1 M H_2SO_4) at a room temperature. The prepared catalysts were also evaluated by X-ray photoemission spectroscopy (XPS) and density functional calculations.

Among the molecules, 1,10-phenanthroline, quinoxaline, and dipyridophenazine on CB showed highest activities, whose onset potentials (potentials versus RHE at a current density of 10 mA cm^{-2}) were 0.29 V, 0.28 V, and 0.21 V, respectively. This tendency suggested that an 1,10-phenanthroline type local structure showed high ORR activities because quinoxaline and dipyridophenazine also contains the same local structure. XPS spectra after the superimposed voltage of 0.2 eV in an ORR condition for 1,10-phenanthroline showed two peaks corresponding to pyridinium N and pyridinic N. This also suggested that N-H…N structure promoted the following ORR reaction. The detail of the effect of the local electronic structure in the adsorbed molecules will be discussed.

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Thin Films Division
Room 104B - Session TF+AM+EM+PS-TuM

Atomic Layer Processing: Area Selective Deposition

Moderators: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, France, Steven George, University of Colorado at Boulder

8:00am **TF+AM+EM+PS-TuM1 New Approaches for Area-Selective Atomic Layer Deposition: Inspiration from Etching**, ***Adrie Mackus,*** Eindhoven University of Technology, The Netherlands, Nederland **INVITED**

While selectivity has always been one of the most important features of an etching process, only in recent years there has been significant interest in selectivity for deposition, motivated by the application of area-selective deposition in self-aligned fabrication. With selective etching being a more mature technology, previous work in etching can serve as inspiration for how to make deposition processes selective. For example, inhibition layers have been employed in etching to obtain selectivity. Similarly, the use of small molecule inhibitors is currently being explored for achieving area-selective atomic layer deposition (ALD).[1]

Moreover, with the recent advancements in atomic layer etching (ALE), new opportunities emerge for selective processing of material based on novel combinations of ALD and ALE. In recent work, ALE cycles have been implemented in area-selective ALD processes to improve the selectivity.[2]

In this presentation, the similarities between etching and area-selective ALD will be described, in order to discuss what the area-selective ALD community can learn from previous work in etching. Recent developments in area-selective ALD will be illustrated by discussing new area-selective ALD approaches based on the use of inhibitors in ABC-type (i.e. three-step) ALD cycles, and on supercycles combining ALD and ALE cycles.

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2. R. Vallat, R. Gassiloud, B. Eychenne, and C. Vallée, *J. Vac. Sci. Technol. A.***35**, O1B104 (2017)

8:40am **TF+AM+EM+PS-TuM3 Nucleation of HfO_2 on Si, SiO_2 and TiN Substrates in PE-ALD Processes Investigated by In situ Ellipsometry and Optical Emission Specroscopy (OES)**, ***Marceline Bonvalot,*** *S. belahcen, V. Pesce, A. Chaker, P. Gonon, C. Vallée, A. Bsiesy,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

It is generally admitted that the physical properties of ultrathin layers elaborated by ALD processes are strongly dependent upon the very initial stages of layer growth, defined as the nucleation step. This nucleation step may for instance affect the cristallinity and the texturation of the material when growing in a crystalline state, it can also significantly contribute to the sharpness of the interface between the substrate and the growing material and/or determine the layer density and surface rugosity. Moreover, this nucleation step also plays a major role in the advancement of Selective Area Deposition Processes (SALD), which are considered, as of today, as a very promising approach for the development of bottom-up routes alternative to increasingly expenseive thin layer patterning processes. In these regards, a good knowledge of the phenomena affecting the nucleation mechanisms in ALD is required.

In this work, the initial stages of layer growth has been investigated during the deposition of HfO_2 by Plasma-Enhanced ALD in a FlexAL set-up equipped with an ALE (Atomic Layer Etching) bias system developed by Oxford. Four types of substrates have been put on trial for this purpose, namely, HF last treated Si(100), SiO_2 (45 nm dry oxide)/Si, SiO_2 (500 nm wet oxide)/Si, and TiN (15 nm ALD)/Si. Several in situ surface treatments have been applied on these substrates, prior to HfO_2 ALD cycles with TEMAH as hafnium precursor. They include exposure to a plasma treatment composed of either Ar, CF_4 and O_2 or any mixture of these gases. A very low power (1-10 W) can be applied on the substrate to allow low DC self-bias voltage, which determines energies of ions extracted from the plasma in the vicinity of the substrate. This bias in turn allows an estimation of the contribution of both chemical and physical plasma-surface interactions to the growth mechanism. The nucleation process is followed in situ by spectroscopic ellipsometry assisted by Optical Emission Spectroscopy for the identification of plasma active species and desorbed by-products.

This presentation will describe how the nucleation time on different substrates can be successfully tuned, either delayed or accelerated, thanks to appropriate in situ surface treatment parameters, without inducing any significant perturbation in the subsequent steady state layer growth. These results will be discussed in view of literature data and potential applications to the development of selective ALD.

9:00am **TF+AM+EM+PS-TuM4 Topographical Selectivity with BN Electron-Enhanced ALD**, ***Jaclyn Sprenger,*** *A.S. Cavanagh, H. Sun,* University of Colorado at Boulder; *A. Roshko, P. Blanchard,* National Institute of Standards and Technology; *S.M. George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) is a new growth technique using sequential self-limiting exposures of electrons and precursor. The electrons produce dangling bonds at the surface through the process of electron stimulated desorption (ESD). The dangling bonds then facilitate the adsorption of precursor resulting in film growth. Because the electron flux is directional, EE-ALD can be used for selective area deposition. For portions of the sample that are masked from the e^--beam, no dangling bonds are produced and no film growth occurs. Additionally, any portion of the surface that is parallel to the e^--beam, e.g. the walls of a trench, may be considered topographically masked because the e^--beam is not incident on the surface.

The topographically selective area deposition by EE-ALD was investigated by depositing boron nitride (BN) EE-ALD films on a trench structure. EE-ALD of BN has been demonstrated using sequential exposures of borazine ($B_3N_3H_6$) and electrons (50-450 eV) at room temperature [1]. GaN [2] and Si [3] have also been deposited earlier using EE-ALD. The topographical selectivity was investigated by growing an EE-ALD BN film on a trench structure. On the vertical walls of a trench structure, aligned parallel to the e^--beam, there should be no electron flux and no film. In contrast, the top and bottom of the trench will receive the full flux of the e^--beam. To test these ideas, high resolution TEM images were recorded after 1000 cycles of BN EE-ALD on a trench structure.

BN films were observed on the top and bottom of the trench. For the trenches used in this study, the side walls were not vertical. Some BN film deposition did occur on these sidewalls, but at a lower growth rate than the horizontal surfaces at the top and bottom of the trench. The electron flux on the side walls was reduced by a factor of cos θ where θ is the angle between the surface normal of trench wall and the e^--beam. Incorporating the reduced electron flux into the model for EE-ALD film growth showed excellent agreement with film thicknesses observed on the trench walls. The topographic selectivity of EE-ALD, demonstrated with BN, coupled with a metal chemistry, would offer a promising solution to challenges such as the bottom-up-fill of conductors in trenches or vias.

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9:20am **TF+AM+EM+PS-TuM5 Optimization by In situ Ellipsometry of ALD and ALE Successive Steps for the Selective Atomic Layer Deposition of Ta_2O_5 on TiN and Si.***, **Vincent Pesce**, C. Vallée,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; R. Gassilloud,* Cea Leti, France*; A. Chaker, M. Bonvalot, B. Pelissier,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; N. Nicolas,* Cea, France*; A. Bsiesy,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

The drastic reduction of microelectronic device dimensions, traditionally achieved through a photolithography process, requires more and more stringent process conditions in this top-down approach. Recent developments in atomic layer deposition processes (ALD) have shown that a new bottom-up approach is possible by the combination of ALD and Atomic Layer Etching (ALE) steps for the selective growth on patterned surfaces [1]. Indeed, it has been shown that the nucleation kinetics in the initial stages of a deposition process is strongly dependent on the chemical state of substrate surfaces. Thus, different nucleation delays can be achieved on patterned substrates, leading to significant variation of thickness in spite of a similar growth rate after nucleation (in the steady state). Prior to precursor deposition, a first step is carried out, which activates or inhibits nucleation sites on patterned substrates. For instance, an O_2/CF_4 plasma treatment leads to the formation of a fluorocarbon polymer, whose thickness depends on the chemistry of the surface: its thickness may be less on Si as compared to TiN, because SiF_4 molecules are more volatile than their TiF_4 counterparts. In turn, this CF_x rich layer can serve as a passivation layer to alter the nucleation sites during the subsequent deposition process. Similarly, an oxidation plasma treatment serves to activate nucleation sites through the formation of metal-oxygen bonds on the patterned substrate, which in turn favors an immediate growth during deposition process.

In this work, we have investigated the impact of both chemical and physical surface interactions during the deposition of Ta_2O_5 in a PE-ALD process. These investigations have been carried out in a FlexAL PEALD tool equipped with an ALE bias system developed by Oxford. A selective deposition super cycle has been defined, which consists in alternating a CF_4 plasma treatment with a Ta_2O_5 ALD deposition cycle with an O_2 plasma as oxidation step. In situ ellipsometry measurements have been used to investigate the impact of ion bombardement and the CF_x layer growth during the optimization of the ALE parameters.

These measurements have been correlated to ex situ XRR and XPS to confirm the thickness on both Si and TiN substrates and analyze the chemistry of the different layers or interfaces.

[1] R. Vallat et al. "Selective deposition of Ta_2O_5 by adding plasma etching super-cycles in plasma enhanced atomic layer deposition steps." *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 35.1 (2017): 01B104. (DOI: 10.1116/1.4965966)

9:40am **TF+AM+EM+PS-TuM6 ALD and PEALD of ZnO on MoS_2 and WSe_2***, **Timothy N. Walter**[1], S. Lee,* The Pennsylvania State Univeristy*; M. Chubarov,* The Pennsylvania State University*; X. Zhang,* The Pennsylvania State Univeristy*; T.H. Choudhury, J.M. Redwing,* The Pennsylvania State University*; T.N. Jackson, S.E. Mohney,* The Pennsylvania State Univeristy

Inducing nucleation on the inherently passivated surfaces of 2D materials such as transition metal dichalcogenides (TMDs) can be challenging for atomic layer deposition (ALD); however, this situation also presents an opportunity for selective growth by ALD. Additionally, ZnO/TMD heterojunctions have favorable band alignments for catalysis and offer possibilities for nanoscale electronic devices including transparent electronics, photodiodes, and piezo-phototronics. This work explores the growth of ZnO on the TMDs MoS_2 and WSe_2 using thermal ALD, thermal ALD with UV-O_3 surface pre-treatment, and plasma enhanced ALD (PEALD). Depositions were performed on both few-layer exfoliated flakes and coalesced single-layer films (with scattered 2- or 3-layer islands) that were already grown by gas source chemical vapor deposition (CVD). Samples were characterized by atomic force microscopy (AFM), Raman spectroscopy, photoluminescence (PL), and X-ray photoelectron spectroscopy (XPS) before and after deposition of ZnO. For both MoS_2 and WSe_2, thermal ALD of ZnO using diethyl zinc (DEZ) and water at 125 °C resulted in a long nucleation delay on the TMD surfaces, showing selectivity against ZnO growth on TMDs compared to the surrounding SiO_2/Si substrate. Even after hundreds of cycles, very little change was detected by XPS, Raman spectroscopy, or AFM; however, nucleation did occur at defects and caused surface roughness to increase. UV-O_3 pre-treatment before thermal ALD yielded different results on MoS_2 compared to WSe_2. UV-O_3 functionalizes MoS_2 for nucleation and subsequent growth of ZnO without destroying the underlying MoS_2; however, UV-O_3 fully oxidized regions of the WSe_2 surface and promoted nucleation. PEALD using DEZ and N_2O on both TMDs resulted in a conformal and smooth film, but it oxidized the top layer of the TMDs according to XPS. In conclusion, UV-O_3 pre-treatment and plasma-enhanced deposition allow for nucleation and growth of ZnO on TMD substrates, sometimes to the detriment of the top layer of material; however, the planar surfaces of 2D materials resist nucleation for hundreds of cycles of thermal ALD.

11:00am **TF+AM+EM+PS-TuM10 From Fundamental Insights into Growth and Nucleation Mechanisms to Area-selective Deposition***, **Annelies Delabie**,* IMEC & KU Leuven, Belgium*; J. Soethoudt,* KU Leuven, Belgium*; G. Pourtois, S. Van Elshocht, K. Barla,* Imec, Belgium*; F. Grillo, E. Marques, J.R. van Ommen,* TU Delft, Netherlands **INVITED**

Area-selective deposition holds the potential to build structures from the bottom up, only where needed, with atomic precision. It is gaining importance for manufacturing of nano-electronic devices as it enables self-aligned deposition for accurate pattern placement and bottom-up deposition in trenches or holes. It can simplify complex integration flows and implies significant cost reduction. The key to area-selective deposition is surface chemistry, as it is based on the surface dependence of deposition techniques like chemical vapor deposition (CVD) and atomic layer deposition (ALD). Today, however, only few industrial processes make use of area-selective deposition, mainly because only few materials can be deposited with sufficient selectivity. In addition, defectivity is a great challenge, as substrate inhibition is often associated with island growth. Detailed insights into the surface chemistry and nucleation mechanisms is essential, as this insight can be used to expand the material combinations accessible by area-selective deposition, as well as to design defect removal strategies. Finally, area-selective deposition is affected by patterning due to changes in surface composition and/or due to diffusion. This illustrates the need for understanding and optimization of the processes in patterns with relevant dimensions. In this work, we review our current understanding of the inherent surface dependence of ALD processes. We show how insight into the growth and nucleation mechanisms of ALD can be applied to enable area-selective deposition with defect removal solutions.

11:40am **TF+AM+EM+PS-TuM12 DETA SAMs as ALD Ru Inhibitor for Area-selective Bottom-up Interconnects***, **Ivan Zyulkov**,* IMEC & KU Leuven*; S. Armini,* IMEC, Belgium*; S. De Gendt,* IMEC, KU Leuven, Belgium

Replacement of Cu interconnects by an alternative metal will be required beyond 32 nm metal pitch in order to decrease the metal line resistance and prevent IC failure due to the Cu electromigration. Based on recent studies, Ru has several advantages when compared to Cu, which make it an attractive candidate for the Cu replacement: i) lower thickness dependence of the resistivity due to a short electron mean free path (6.6/4.9 nm for Ru vs 39.9 nm for Cu), ii) higher melting temperature (2334 ºC for Ru vs 1032 ºC for Cu) which represents better Ru resistance to electromighration and iii) possibility of integration without a diffusion barrier, resulting in a larger effective metal area. However, conventional electrochemical and electroless deposition methods used in IC manufacturing are not available for the Ru metallization. Additionally, downscaling of the metal structures down to 10 nm causes metal lines filling issues even using conformal ALD, since seams are likely to be formed due to trench pinch-off. As a solution, area selective deposition (ASD) can be exploited, allowing bottom-up and void-free filling of high aspect ratio structures. In addition, ASD of Ru can find application in advanced patterning schemes.

This work is focused on ASD of Ru in a via area of the interconnect structure. In this case ALD selectivity to metallic via bottom (underlying metal line) should be achieved with respect to organosilicate glass (OSG) via sidewalls. In this work, thermal ALD Ru using an ethylbenzene-ethyleyelohexadiene (EBECHRu) precursor with O_2 co-reactant was used. The precursor molecule has ethyl-cyclohexadienyl ligands, which are expected to show a preferential interaction/ inhibition with specific surface groups. In order to passivate the hydroxy-terminated OSG sidewalls against the Ru deposition different siloxane derived self-assembled monolayers (SAMs) were used. According to RBS and SEM analysis, (3-trimethoxysilylpropyl)diethylenetriamine (DETA) SAMs provide more than 300 cycles inhibition of the ALD Ru growth on Si oxide and OSG. XPS, FTIR and spectroscopic ellipsometry on the SAM film before and after ALD are compared in order to identify relevant selectivity mechanisms. In order to prevent DETA passivation of the Cu interface where ALD Ru is expected to

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[1] **TFD James Harper Award Finalist**

grow for the bottom-up via fill, undecanethiol (UDT) SAMs were used as a selective sacrificial Cu protection before the DETA deposition. The thiol SAMs can be removed from the Cu surface at 250 ºC while silane (DETA) is stable on the dielectric surface at temperatures above 350 ºC and higher. The double SAM and area selective bottom-up ALD Ru tested in 45 nm half-pitch lines will be presented.

Thin Films Division
Room 102A - Session TF+AS-TuM

Special Session in Honor of Paul Holloway: Luminescent Materials Growth, Synthesis and Characterization

Moderators: Sean Jones, National Science Foundation (NSF), Jay Lewis, Defense Advanced Research Projects Agency

8:00am **TF+AS-TuM1 INTRO: Special Session Honoring Professor Paul H. Holloway***, **Gary McGuire**,* Adamas Nanotechnologies

In light of Professor Holloway's many contributions to the AVS and Thin Film Division special recognition will be given to him during a session dedicated to highlighting his prominence as an educator, scientist and leader. Professor Holloway has held many positions within the AVS including AVS President in 1987, Fellow 1993, Honorary Member 1997, Albert Nerken Award Winner, 1999. The Paul H. Holloway Young Investigator Award is given each year by the Thin Film Division to a deserving recipient. During his career he made major contributions to surface science and surface analysis. His research covered a diverse range of luminescent materials including thin film and powder phosphors, organic light emitting diodes, quantum dots and nanocrystals.

8:20am **TF+AS-TuM2 Harnessing Disorder in Detectors***, **Jay Lewis**,* Defense Advanced Research Projects Agency

Most progress in optoelectronic devices has been built upon increasingly perfect materials, where "perfect" implies reducing impurities, point defect, dislocations, and grain boundaries. However the properties of quantum dot devices, such as those demonstrated by the Holloway group, are largely dominated by the surfaces of the nanocrystals. This paper explores the role of nanostructured devices through the lens of DARPA's Wafer Scale Infrared Detectors (WIRED) program, which seeks to develop infrared detector technology that is inherently disordered. Disorder is a byproduct of the program objective to process detectors directly onto the silicon wafers that are used to process and read out the signals. The program is exploring polycrystalline materials deposited by chemical bath deposition, quantum dot materials deposited by spin or dip coating, as well as traditional III-V compounds deposited at low temperatures compatible with complementary metal oxide semiconductor (CMOS) circuitry. These results are presented in the context of the broader portfolio of DARPA programs seeking to advance the state of the art in imaging and sensing technology.

8:40am **TF+AS-TuM3 Luminescent Materials for Solid State Lighting and Solar Cell Applications***, **Hendrik C Swart**, J.J. Terblans, R.E. Kroon, E. Coetsee, M.M. Duvenhage, E. Hasabeldaim, A. Balakrishna, A. Kumar,* University of the Free State, Republic of South Africa*; P.H. Holloway,* University of Florida **INVITED**

Luminescent compounds and materials have numerous uses. The emission properties, whether of a fast decay rate fluorescent material or a slow decay rate phosphorescent material, are defined by the chemical composition and the physical structure of the luminescent material. The crystal field that is determined by the environment in the host material in combination with the various dopant ions with the correct valence state can be used to obtain emissions from the Ultra violet (UV) to the infra-red (IR) wavelength ranges. Phosphor materials have been successfully used to improve the efficiency of various applications. Nanoparticles both undoped and doped with different rare earth elements were synthesized by several synthesized techniques. The major problem that limits solar cells' efficiency is their insensitivity to the whole solar spectrum which is the so-called spectral mismatch. Therefore, several mechanisms have been explored based on photoluminescence (PL) to convert the solar cell spectrum where the spectral response of the solar cell is low to regions where the spectral response of the solar cell is high. For single crystalline silicon (Si) photovoltaic (PV) cells with a rather small semiconductor band-gap (Eg: 1.12 eV, corresponding to a wavelength of ~1100 nm), the transmission loss of the sub-band-gap photons can still amount to about 20% of the sun's energy irradiated onto the Earth's surface. For PV cells with a larger band-gap, such as amorphous Si (Eg: 1.75 eV) solar cells, which are limited to absorb sunlight with wavelengths below 708 nm, manifest even higher near infrared transmission losses. Downconversion, up-conversion (UC) and downshifting are some of the mechanisms that may be applied to improve the spectral response. Upconversion nanoparticles (UCNPs) have shown some promising possibilities to be considered in this respect, however, low UC efficiency of UCNPs is still the most severe limitation of their applications. In downshifting the strong deep level emission (DLE) and near band edge emission could be tuned to cover a wide spectral range. The strong DLE, covering a wide spectral range of ~375-650 nm, signifies the potential optoelectronics application in the near white LED applications. Degradation of the different phosphors during prolonged electron/photon bombardment also played a vital role in their possible applications. Examples of different phosphor materials with different applications such as Solid State Lighting will be shown.

9:20am **TF+AS-TuM5 Fluorescent Nanodiamond for Applications in Whole Body Imaging***, **Olga Shenderova**, M.D. Torelli,* Adamas Nanotechnologies*; A. Rickard,* Duke University*; N.J. Nunn,* Adamas Nanotechnologies*; M. Backer,* SibTech*; G.M. Palmer,* Duke University*; G. McGuire,* Adamas Nanotechnologies **INVITED**

Fluorescent nanodiamonds (FNDs) containing color centers exhibit distinct properties including very high biological compatibility, infinite photostability, absence of photoblinking, long fluorescence lifetime (>10 ns), and ease of biofunctionalization, which makes them an attractive alternative to quantum dots, organic dyes, and polymer beads as imaging reagents. Potential applications include background-free and long-term cell imaging, flow cytometry, super-resolution imaging, correlative microscopy, labeling of low-abundance cellular components, fiducial markers, and image guided surgery. In this talk, after reviewing unique properties of FND, their utility for in vivo tumor imaging will be presented. To target receptors overexpressed in cancerous tissue, FNDs were functionalized with vascular endothelial growth factor (VEGF) via click chemistry and then validated *in vitro* for functional activity. Thereafter, FND-VEGF was administered via tail vein injection to nude mice induced with a mammary carcinoma, and mice were analyzed both in vivo and ex vivo via whole body imaging and fluorescence microscopy. Ex vivo micro-spectroscopy utilized the unique spectral signature of nitrogen-vacancy induced fluorescence to demonstrate unambiguous determination of ND translocation to tumorous tissue. The results are placed in the context of FND for whole-body imaging and related applications.

11:00am **TF+AS-TuM10 The Apple does not Fall Far from the Tree: A Serendipitous Journey from Luminescent Materials to Nanoscale Focused Electron (and Ion) Beam Induced Processing***, **Philip D. Rack**,* University of Tennessee Knoxville **INVITED**

I graduated from Paul Hollloway's group at the University of Florida in 1997 where I studied luminescent materials for electroluminescent displays. If the saying is true that "imitation is the sincerest form of flattery," then my career speaks volumes of my admiration for the man I had the privilege to call my Phd advisor. In this talk, I will briefly overview some of the luminescent materials research that my group has performed over the years. In true Holloway fashion, I will overview my groups serendipitous journey from luminescent materials to focused nanoscale electron beam induced processing. The remainder of the talk will review topics near and dear to Dr. Holloway's heart, electron(ion)-gas-solid interactions, and illustrate that appropriate understanding of these interactions can result in the directed growth/etching at the nanoscale. I will overview our groups Monte Carlo simulation to illustrate some of the critical electron(ion)-gas-solid interactions that can rate and resolution limit the deposition and etching processes. Next, I will show how a synchronized pulsed laser can photothermally assist both the etching and deposition processes. Finally, I will review our recent research direction in this area, which is controlled 3d nanoscale printing. Along the way, I will recall anecdotes that illustrate principles learned from the "Holloway way" and hopefully illustrate that I am an apple that did not fall far from the Holloway tree.

11:40am **TF+AS-TuM12 Atomic Layer Deposition of Optoelectronic Materials***, **Markku Leskela**, M.K. Ritala,* University of Helsinki, Finland **INVITED**

In optoelectronics, i.e. in electronic devices and systems that emit, detect and control light, the active materials are usually II-VI or III-V semiconductors. Historically in Atomic Layer Deposition (ALD) or Atomic Layer Epitaxy (ALE) as it was called in 70s and 80s, zinc sulfide has been very important material. The ALE technology was developed for manufacturing AC driven thin film electroluminescent displays [1]. Monochromic yellow-black displays based on ZnS:Mn luminescent layer sandwiched between dielectrics and electrodes has been manufactured industrially by ALD continuously since 1984. Besides the luminescent layer, the high-quality oxide layers made by ALE have had an important role as dielectrics and passivation layers in the success of the ACTFEL displays. Multicolor displays can be realized by filtering the broad emission band of ZnS:Mn or using other luminescent material, e.g. green-emitting ZnS:Tb. Despite of intense studies in 1980s and 1990s full-color ACTFEL devices could not been developed to the mass production level because of the missing efficient deep blue-emitting phosphor. Today the strongest developing application area in thin film EL displays is transparent displays used widely in different vehicles [2]. This motivates to re-examine the color displays.

Deposition of epitaxial films of III-V materials is possible with ALD as demonstrated already in 1985 [3]. Processes have been developed for all III-V materials using alkyl compounds for group III metals and hydrides for group V elements as precursors. The advantages of ALD processing compared to MOCVD or MBE have remained, however, modest because of the carbon contamination.

Transition metal dichalcogenides are emerging 2D materials that are potential channel materials in field-effect transistors as well as phototransistors and other optoelectronic devices. The bottle-neck in the large use of these two-dimensional materials is the lack of scalable, low-temperature process for high-quality, large-area films. ALD has been studied as a solution for these problems [4].

In other optoelectronic devices the ALD films find most often use in passivation and encapsulation. Silicon based solar cells is a good example of the former [5] and OLED displays from the latter application area [6].

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Thin Films Division
Room 101A - Session TF-TuM

Emerging Applications for ALD

Moderators: Arrelaine Dameron, Forge Nano, Qing Peng, University of Alabama

8:00am **TF-TuM1 Atomic Layer Deposition of the Metal Pyrites FeS_2, CoS_2, and NiS_2**, ***Xinwei Wang***, Shenzhen Graduate School, Peking University, China

The pyrite-type transition-metal disulfides (MS_2, M = Fe, Co, Ni) form a series of compounds that are highly interesting in many aspects. These compounds share the same cubic pyrite crystal structure but differ in the progressive increase of an anti-bonding *d* electron in the conduction band, and as a result, the metal pyrites exhibit very diverse and intriguing electrical magnetic properties from diamagnetic semiconductive to itinerant-electron ferromagnetic and to antiferromagnetic semiconductive. This diversity of the material properties has not only offered a model system platform for fundamental science studies but also enabled tremendous engineering possibilities for practical applications, such as solar cells, lithium/sodium-ion batteries, and electrocatalytic hydrogen evolution, oxygen evolution, and oxygen reduction.

In this presentation, we will show our latest progress on the development of atomic layer deposition processes for the metal pyrites of FeS_2, CoS_2, and NiS_2 (*Angew. Chem.Int. Ed.* 2018, doi:10.1002/anie.201803092). We use the metal amidinate compounds as the precursors for the metals and H_2S plasma as the sulfur source, and we will show that the deposition processes for FeS_2, CoS_2, and NiS_2 all follow ideal layer-by-layer ALD growth behavior over a wide temperature range to produce fairly pure, smooth, pyrite-structure metal disulfide films. We will further show that the ALD FeS_2, CoS_2, and NiS_2 films can be conformally deposited into deep narrow trenches with aspect ratios as high as 10:1, which thereby highlights the broad and promising applicability of these ALD processes for conformal film coatings on complex high-aspect-ratio 3D architectures in general.

8:20am **TF-TuM2 Atomic Layer Deposition of Yttrium Fluoride and Yttrium Oxyfluoride Films with Tunable Stoichiometry**, ***Jasmine Wallas***[1], *J.A. Murdzek, D.K. Lancaster, A.S. Cavanagh, S.M. George,* University of Colorado at Boulder

YF_3 and YO_xF_y are materials with excellent chemical and thermal stability. YF_3 and YO_xF_y have both demonstrated exceptional corrosion resistance to highly reactive plasmas. In this work, YF_3 atomic layer deposition (ALD) was developed using tris(butylcyclopentadienyl) yttrium and HF-pyridine as the reactants. The ALD of YO_xF_y alloys was also demonstrated with tunable control of the oxygen and fluorine stoichiometry. This tunable control was difficult because of the rapid exchange of oxygen by fluorine in Y_2O_3 and YO_xF_y alloys during HF exposures.

In situ quartz crystal microbalance (QCM) analysis of YF_3 ALD revealed linear mass changes and self-limiting behavior using tris(butylcyclopentadienyl) yttrium and HF-pyridine as the reactants. The mass gain per cycle (MGPC) was 21.5 ng cm^{-2} at 225°C. The growth rate of YF_3 ALD was also determined to be 0.3 Å per cycle by ex situ X-ray reflectivity analysis. Energy dispersive spectroscopy (EDS) of a cross-section of the YF_3 film yielded a uniform 3:1 ratio of F:Y with low impurities.

YO_xF_y alloys were deposited using H_2O together with the tris(butylcyclopentadienyl) yttrium and HF-pyridine reactants. However, control of the composition of the YO_xF_y alloys was complicated by the facile exchange of oxygen by fluorine during the HF exposures. The oxygen/fluorine exchange was most obvious during HF exposures on Y_2O_3 ALD films when a large mass gain was observed during fluorination. The Y_2O_3 fluorination reaction is believed to be: $Y_2O_3 + 6\ HF \rightarrow 2\ YF_3 + 3\ H_2O$. In addition to the large mass gain, the presence of fluorine throughout the entire film was revealed by X-ray photoelectron spectroscopy (XPS) measurements with depth-profiling. The XPS depth-profiling results are consistent with rapid fluorine diffusion in the Y_2O_3 and YO_xF_y films.

Various super-cycles were employed to obtain YO_xF_y alloys with particular F:O ratios. The most reliable method for composition control was defined by performing HF exposures between intervals of Y_2O_3 ALD. The number of Y_2O_3 ALD cycles and the length of the HF exposure could be varied to produce YO_xF_y alloy films with tunable and consistent composition as measured with XPS depth-profiling. The growth rate of the YO_xF_y alloy films was dependent on the number of Y_2O_3 ALD cycles before the HF exposures. The super-cycles with a larger number of Y_2O_3 ALD cycles before the HF exposures produced higher growth rates resulting from the higher growth rate of 0.8 Å per cycle for Y_2O_3 ALD.

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8:40am **TF-TuM3 Synthesis of Single Phase Two-dimensional SnS_2 by Plasma-enhanced Atomic Layer Deposition**, *J.J. Pyeon, I.-H. Baek,* Korea Institute of Science and Technology*; T.-M. Chung,* Korea Research Institute of Chemical Technology*; J.H. Han,* Seoul National University of Science and Technology*; C.-Y. Kang,* ***SeongKeun Kim,*** Korea Institute of Science and Technology, Republic of Korea

Two-dimensional (2-D) metal chalcogenides have received great attention because of their unique characteristics. A challenge in implementing 2-D metal chalcogenides in emerging devices is to synthesize a well-crystallized layer over large areas at temperatures compatible with current fabrication processes. Tin disulfide, a n-type layered semiconductor, is a promising candidate for realizing large-area growth at low temperatures because of its low melting point. However, tin sulfides exist in various phases such as SnS, Sn_2S_3, and SnS_2. It is challenging to form a single phase SnS_2 at low temperatures.

Here, we demonstrated the synthesis of high-quality SnS_2 by plasma-enhanced atomic layer deposition (PEALD). All the processes were performed below 300 ^{o}C, which is compatible with current electronic devices. Stoichiometric SnS_2 films were formed. It was verified from various techniques such as Raman spectroscopy, x-ray photoelectron spectroscopy, and x-ray diffraction that a single phase of SnS_2 was formed. It was found that the microstructure of the SnS_2 films was strongly dependent on the growth temperature. Vertically aligned SnS_2 flakes were observed in the SnS2 grown at relatively high temperatures (210 - 270 ^{o}C). Through a two-step process – a seed layer growth at low temperature (150 ^{o}C) and a main layer growth at high temperatures (240 – 270 ^{o}C), well crystallized SnS_2 layers were aligned in parallel to the substrate. Moreover, the properties of field-effect transistor using the SnS_2 films were investigated. A high on/off ratio of ~ 10^6 and a moderate field-effect mobility of ~ 1 cm^2/Vs were achieved from the devices utilizing SnS_2 grown by PEALD.

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[1] **TFD James Harper Award Finalist**

9:00am **TF-TuM4 Phase Selective, Low Temperature Growth of TiO2 by Atomic Layer Epitaxy*, Jason Avila*,** *D.R. Boris, S.B. Qadri, J.A. Freitas, S.G. Walton,* U.S. Naval Research Laboratory*; C.R. Eddy, Jr.,* U. S. Naval Research Laboratory*; V.D. Wheeler,* U.S. Naval Research Laboratory

Atomic layer deposition (ALD) of TiO_2 has been widely explored recently due to its promise in non-volatile resistive switch, high-k gate dielectric, solar cell, and photocatalytic applications. This growth method has become increasingly useful as device dimensions are reduced and non-planar complexity is increased. To facilitate epitaxial films at low growth temperatures (T_g), many have investigated plasma, laser or photon, or electron enhanced ALD processes. Specifically for TiO_2, it would be beneficial to selectively grow epitaxial anatase or rutile phases in order to tailor optical, catalytic and electrical properties for the required application. Typically, TiO_2 phase selectively is attained by varying the underlying substrate, Ti and/or oxidation precursor, or T_g. However, here we demonstrate phase selectivity of high quality epitaxial TiO_2 films simply by adjusting plasma gas composition, pressure and Tg.

A Veeco Fiji G2 reactor was used to deposit TiO_2 films on different sapphire orientations (c-, m-, a-) with tetrakis(dimethylamido)titanium (TDMAT) and either Ar/O_2 or pure O_2 plasma at 100-350° C. Previous reports indicate that tuning the ion energy, specifically through substrate biasing, can influence TiO_2 film crystallinity and phase [1]. The high pumping speed and large gas flow range available in this specific ALD system provides a wide variation in operating pressures (7-100's mTorr), which effectively allows tuning of plasma characteristics. Operating at relatively low pressures (9-21mTorr) resulted in a significant flux ($0.5\text{-}1.5\mathrm{x}10^{19}$ $m^{-2}s^{-1}$) of energetic ions (30-50eV), with both the flux and energy decreasing as the pressure is increased. The low pressure conditions yield high-quality epitaxial films at all temperatures, which differs from previous reports using these specific precursors [2,3] likely due to these unique plasma conditions.

Gas composition during the plasma step also had a substantial effect on growth rate, TiO_2 phase, and strain. At T_g < 300° C, the growth rate was increased from 0.5 to 0.7 Å /cycle by switching from Ar/O_2 to pure O_2. Moreover, an O_2 plasma produced only rutile TiO_2 films, with less strain, independent of growth temperature or underlying substrate orientation. In contrast, films deposited with an Ar/O_2 plasma show a phase dependence on temperature and substrate. Films on c-plane Al_2O_3 go from anatase at T_g below 200° C to rutile above 300° C. The films on m-plane Al_2O_3 are rutile independent of temperature.

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9:20am **TF-TuM5 Substrate Biasing During Plasma Atomic Layer Deposition: From Stress-controlled Oxides to Low-resistivity Nitrides*, Harm Knoops,*** Oxford Instruments, The Netherlands*; T.F. Faraz, K. Arts, S. Karwal, M.C. Creatore, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Thin films grown by plasma atomic layer deposition (ALD) can be strongly influenced by the energy of the ions present during the plasma step. Here we report on how using enhanced energies influence the material properties of many oxides and nitrides.[1,2] To utilize these effects, discussion on promising process schemes and which material properties are key is needed. This work will discuss application relevant aspects and focus on the stress-control of oxides and the reduction of resistivity for nitrides.

Ion energy control during plasma exposure was carried out in a commercial 200-mm remote plasma ALD system (Oxford Instruments FlexAL) equipped with RF substrate biasing. Substrate biasing increased the refractive index of TiO_2 at 300 °C to 2.54±0.03, mass density to 4.2±0.2 g/cm^3, and the crystal phase went from anatase to rutile. ALD of TiO_2 at 150 °C typically yields amorphous films, but using a bias crystalline rutile phase was obtained. Besides these modified material properties the residual stress was altered from tensile (176±50 MPa) to strongly compressive (-2430±50 MPa) and by choosing the bias voltage and duration, a close to zero stress could be achieved (−25±50 MPa). Stress control of oxides on planar surfaces can be beneficial for several devices through: anti-reflective TiO_2 coatings, stressed Al_2O_3/HfO_2 gate oxides, and compressive Ta_2O_5 barrier layers.

For transition metal nitrides, enhancing ion energies was observed to have pronounced effects on chemical composition and microstructure.[1,2] Energetic ion bombardment lowered film resistivity down to 139±10 μΩcm at -187V bias for TiN and increased the crystallinity. The ability to deposit crystalline films on temperature sensitive substrates (e.g., conductive TiN on polymer substrates) could be a benefit for low temperature electronics. Oxygen impurity content was observed to be significantly reduced by substrate biasing. Oxygen contents of 3±2 at. % for TiN and <2 at. % for HfN_x were achieved without taking special care of low oxygen backgrounds. Ar/H_2 plasma with biasing was found to allow removal of surface oxygen, while simply extending the plasma exposure without applying bias did not lead to such removal. The reduction of oxygen content by these plasmas also suggests a possible use in applications as a chemical sputter clean of surfaces. In general the application of biasing brings the processing of plasma ALD closer to the realm of ALE and atomic scale processing. Possible related processing schemes and the general trends for nitrides and oxides will be discussed.

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9:40am **TF-TuM6 Development of Novel Superconducting ALD Films for Astronomy Applications*, Frank Greer*,** *P. Day, B. Eom, H. Leduc,* Jet Propulsion Laboratory, California Institute of Technology

Future sub-millimeter telescopes and spectrometers have the potential to revolutionize our understanding of the formation of the modern universe. Sub-millimeter astronomy can probe the fine structure of the cosmic microwave background, giving glimpses into the early universe immediately following the Big Bang. Recent advances in design have enabled the production of large arrays of cryogenically cooled superconducting detectors with sufficient sensitivity for photon counting applications. Transition edge sensors (TES) and other types of detectors, fabricated from thin films of metal nitrides such TiN, NbN, TaN, VN, and their mixtures, are cryogenically cooled to just below their superconducting transition temperature. Photons in the X-ray or sub-millimeter wavelength range can be detected because their absorption will cause the temperature of an appropriately designed TES array element to rise just enough to cause it to have a finite resistance. However, while conventional deposition processes such as physical sputtering have been sufficient for small area arrays and proof of concept sensors, critical parameters such as the superconducting transition temperature are strongly sensitive to film thickness, stochiometry, and interface quality. Therefore, as the size of an individual detector array or the number of detector arrays on a wafer increases, it becomes more and more difficult to fabricate them with sufficiently uniform response in sufficient quantity to populate the focal plane of a large telescope. We are utilizing the uniformity and compositional control provided by atomic layer deposition to overcome these limitations for the fabrication of transition edge sensors as well as other applications requiring superconducting thin films.

11:00am **TF-TuM10 Atomic Layer Deposition of Cobalt Nanoparticles*, Gerben van Straaten,*** *W.M.M. Kessels, M.C. Creatore,* Eindhoven University of Technology, The Netherlands

Cobalt nanoparticles (NPs) with well-defined sizes are highly sought after for a variety of catalytic processes. For example, cobalt NP catalysts for the Fischer-Tropsch process, used in industry to upgrade coal and natural gas into fuels, show a sharp maximum in activity for a particle diameter of ca. 8 nm[1]. Such size-sensitive catalytic processes require conformal deposition of cobalt NPs throughout porous substrates, requirements that can potentially be met by ALD.

ALD of catalytic platinum-group metal NPs with narrow size distributions has been exhaustively studied. However, compared to these systems, ALD of cobalt metal NPs is much more challenging due to their high reactivity. To our knowledge, Co NPs have only been obtained by reduction of ALD-deposited Co_3O_4 NPs [2] or by reduction and subsequent melting of ALD-deposited Co_3O_4 layers [3].

In this contribution, we demonstrate for the first time the direct deposition of Co NPs using Plasma-Enhanced ALD (PEALD)[4]. Cobaltocene ($Co(C_5H_5)_2$) is evaporated at 80°C and dosed for 6s onto an SiO_2 surface held at 250°C. Then, exposure to a remote, inductively coupled plasma fed with NH_3 ($1*10^{-2}$ mbar, 100W) takes place for 10s. After each step, 4s of purging takes place, and saturation of all steps was verified with in-situ Spectroscopic Ellipsometry (SE). By means of TEM we find that Co NPs synthesized via this process consist of a metallic core and an oxide shell formed by air exposure, and that their growth takes places in 3 stages. In the initial stage, up to 150 cycles, a homogeneous coverage of small NPs occurs, with an average diameter of less than 1 nm. Then, after 150 cycles, a second population of larger NPs starts to develop, which increase rapidly in size while retaining a narrow size distribution. After ca. 250 cycles this secondary population is fully developed, with a mean diameter of 7.5 nm and a width of 1.7 nm, but the initial population of small NPs remains, yielding a bimodal size distribution. Growth of this secondary population continues up to ca. 550 cycles, at which point we find from in-situ SE that the NPs coalesce into a continuous film. Preliminary GIXRD and XPS analysis reveals that this film consists of crystalline β-Co but that up to 10 at% of C and N can be present in the film.

Experiments are ongoing to test the catalytic activity of Co NPs synthesized via this method towards the Fischer-Tropsch reaction.

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11:20am **TF-TuM11 Atomic Layer Deposition of Ni-Al-O Catalysts for Water Oxidation***, **Jon Baker**, J.R. Schneider, J.A. Singh, A.J. Mackus, S.F. Bent,* Stanford University

Electrical energy storage has emerged as an important challenge for societies moving away from fossil fuels toward more renewable sources (e.g. solar and wind) that are intermittent in nature. To rely only on solar and wind for electricity, large scale energy storage systems are required. Among several potential solutions, one promising strategy is to store excess electrical energy in the form of chemical bonds, through electrochemical production of fuels. In particular, electrochemical water splitting enables the production of hydrogen gas as a chemical fuel from excess electrical energy. However, a major drawback of this strategy is the low efficiency of the oxygen evolution reaction (OER).

To improve the efficiency of the OER, understanding why certain catalysts perform well is a powerful tool in designing new catalysts with better properties. Atomic layer deposition (ALD) has emerged as a strong platform to study catalysts due to its ability to deposit films that are compositionally well-defined. For electrochemical systems, ALD has the added benefit of high uniformity, conformality and precise thickness control; these attributes can minimize potential confounding effects like resistive and mass transport losses, which may affect measurement of a catalyst's intrinsic activity. In this work, we study the effect of aluminum on Ni-Fe-OOH catalysts. While Ni-Fe-OOH catalysts have been reported to have high activity for the OER (nearly independent of synthesis method), the impact of aluminum on this catalyst is not yet well understood, with a wide range of OER activities reported. By using ALD, ternary films of Ni-Al-O were deposited. Introduction of iron was achieved through electrolyte iron-doping, enabling the formation of the quaternary Ni-Al-Fe-OOH catalyst. Electrochemical characterization of sufficiently thin films found that aluminum improved the turnover frequency of Ni-Fe-OOH catalysts by a factor of 3-4. By carefully controlling composition of the catalyst, the effects of aluminum and iron were independently studied. In iron-free catalysts, aluminum was found to improve OER activity; however, its improvement in activity was small compared to the effect of iron. In addition, thickness dependent studies were performed to understand how morphology and synthesis method may impact observed activity. For Ni-Al-Fe-OOH catalysts, a strong thickness dependence in the OER activity was observed. Characterization of the catalysts *ex situ* and under OER operating conditions reveal the likely cause of this thickness dependence is the observed changing morphology of the film with increasing thicknesses.

11:40am **TF-TuM12 Atomic Layer Deposition of Bismuth Vanadate Photoanodes***, **Sudarat Lee**, A.R. Bielinski, S.L. Esarey, J.J. Brancho,* University of Michigan, Ann Arbor*; B.M. Bartlett,* University of Michigan, Ann Arbor*; N.P. Dasgupta,* University of Michigan, Ann Arbor

Bismuth vanadate (BVO) has been widely studied as one of the most promising photoanode materials for photoelectrochemical (PEC) water splitting, owing to a bandgap of 2.4 eV and favorable band positions for water oxidation. However, while BVO has the potential for high anodic photocurrents, it is often limited by electron-hole separation, charge transport, and water oxidation kinetics, requiring development of nanostructured electrode architectures to optimize performance.

Here we demonstrate a new method for fabricating tunable BVO photoanodes deposited by atomic layer deposition (ALD). We present the first deposition of ALD BVO using $Bi(OCMe_2iPr)_3$ as the bismuth source, vanadium(V)oxytriisopropoxide as the vanadium source, and water as the oxidant. The choice of this recently developed Bi precursor provides full control of Bi:V stoichiometry in contrast to the use of earlier Bi precursors such as triphenylbismuth[1], while also providing a per cycle growth rate that is more than three times higher than previous reports.

The BVO films were deposited as a nanolaminate of binary bismuth and vanadium oxides. The films were post-annealed to achieve the photoactive monoclinic $BiVO_4$ phase. Film composition and photocurrent were investigated as a function of deposition pulse ratio and film thickness. The photoactivity of planar ALD BVO was measured in a three-electrode cell under simulated AM1.5G illumination. Sulfite oxidation was used to optimize the BVO deposition conditions independent of co-catalyst performance.We achieved the highest reported photocurrent to date for ALD photoanodes. Using a planar electrode with a 40nm thick BVO film, a photocurrent of >2.6 mA cm^{-2} at 1.23 V_{RHE} was demonstrated for sulfite oxidation and a photocurrent of >1.1 mA cm^{-2} at 1.23 V_{RHE} was demonstrated for water oxidation using an un-optimized cobalt co-catalyst.

ALD provides conformal coverage of high aspect ratio structures. The development of an ALD process for BVO enables core-shell architectures that help address the charge transport and carrier separation challenges by decoupling carrier diffusion and light absorption lengths. To demonstrate this benefit, BVO was deposited on mesoporous tin oxide (ITO) substrates to form 3-D electrode architectures with tunable absorption and charge extraction properties. The photoresponse was enhanced for both sulfite and water oxidation under illumination, demonstrating the power of ALD to improve light absorption and charge extraction in 3-D nanostructured electrode architectures.

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2016, *9* (13), 1727- 1735.

12:00pm **TF-TuM13 ALD of Cobalt Phosphate Electro-catalyst for Oxygen Evolution Reaction***, **Valerio Di Palma**,* Eindhoven University of Technology, The Netherlands*; G. Zafeiropoulos, M.N. Tsampas,* DIFFER*; W.M.M. Kessels, M.C. Creatore,* Eindhoven University of Technology, The Netherlands

Sunlight-driven water splitting is widely investigated through studies addressing both the development of earth-abundant element-based (photo)electrodes, as well as engineering of compact, efficient and inexpensive devices. One important reason that keeps these systems from being of practical use to date is the sluggish kinetics (high overpotential) of the oxygen evolution reaction (OER). OER is a four electron-proton coupled reaction, while hydrogen evolution reaction (HER) is only a two electron-transfer reaction, and hence usually OER requires a higher overpotential [1].

Electro-deposited cobalt phosphate (CoPi) has been reported as a valid OER catalyst (as bare electrode or as cocatalyst in photoelectrodes) and alternative to rare element compounds [2]. In parallel, ALD is rapidly reaching out also to (photo-)electrocatalytic applications [3,4] and in the present contribution we investigate CoPi growth by ALD and its application as OER catalyst. Compared to electrodeposition, ALD offers the major advantage of tuning the electro-catalyst chemical composition, as we demonstrate in this work.

The CoPi process has been developed using an ABCD scheme, where A, B, C and D are the cobaltocene (CoCp), first oxygen plasma (5 s), trimethylphosphate (TMP) and second oxygen plasma (2 s) dosing steps, respectively. The deposition performed at $300^{o}C$ results in a growth per cycle of about 1.1 Å, determined by in-situ spectroscopic ellipsometry. Elemental characterization by XPS of the ALD prepared CoPi shows a stoichiometry of $Co_3(PO_{4.3})_2$. The film deposited on FTO/glass is active for OER, as confirmed by cyclic voltammetry. The current density peak measured is about 1.0 mA/cm^2 at 1.4 V vs. NHE (Normal Hydrogen Electrode), comparable to the values reported in literature for electrodeposited CoPi. Furthermore, we investigated the effect of Co-to-P concentration ratio on the OER catalytic activity. To this purpose, the process was modified from the aforementioned ABCD approach into an $(AB)_x(CD)_y$ supercycle approach. The sample prepared with a ratio x-to-y of 12-to-11 showed already a higher current density peak (about 1.2 mA/cm^2 at 1.4 V vs NHE) than the sample deposited without the use of supercycles. This finding highlights the role of Co-to-P concentration ratio on the activity of the catalyst and how the ALD supercycle approach can be adopted to this purpose.

References

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[3] A. Paracchino et al., Energy Environ. Sci., 5 (2012) 8673

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Vacuum Technology Division
Room 203B - Session VT-TuM

Large Vacuum Systems and Accelerator Vacuum Technology

Moderator: Yevgeniy Lushtak, SAES Getters USA

8:00am **VT-TuM1 Design of Vacuum Control System for the Linac Coherent Light Source II (LCLS-II) at SLAC National Accelerator Laboratory***, **Shweta Saraf**, S. Kwon, G. Lanza, D. Gill,* SLAC National Accelerator Laboratory **INVITED**

The LCLS-II (Linac Coherent Light Source II), a revolutionary new X-ray laser, is currently being built at SLAC National Accelerator Laboratory. The LCLS-II Vacuum System consists of a combination of particle free and non-particle free areas and includes the beamline vacuum, RF system vacuum, cryogenic system vacuum and supporting systems vacuum. The Vacuum Control System includes the controls and monitoring of different types of gauges, pumps and residual gas analyzers (RGA). The Vacuum Control System uses Allen Bradley PLC (Programmable Logic Controller) to perform interlocking to isolate bad vacuum areas. In particle free areas, a voting scheme is implemented for slow and fast shutter interlock logic to prevent spurious trips. Additional auxiliary control functions and high level monitoring of vacuum components is reported to global control system via an Experimental Physics and Industrial Control System (EPICS) input output controller .This paper will discuss the design and status of the LCLS-II Vacuum Control System.

8:40am **VT-TuM3 Vacuum System Design for Advanced Light Source Upgrade (ALS-U)***, **Sol Omolayo**,* Lawrence Berkeley Lab, University of California, Berkeley

A project is underway to upgrade the existing Advanced Light Source (ALS) synchrotron. The goal of the project is to lower the horizontal emmitance to <75pm resulting in a 2 orders of magnitude increase in soft x-ray brightness. The design utilizes a multi-bend achromat (MBA) lattice which requires a small magnetic aperture of about 24mm. Consequently the vacuum aperture is very small down to 6mm in some areas. This narrow posses a challenge to the vacuum design due to the conductance limitation and space constraints for vacuum chambers. We present the conceptual vacuum design for the ALS-U.

9:00am **VT-TuM4 Vacuum System for CHESS-U: Design, Manufacturing, and Installation***, X. Liu, D.C. Burke, A.T. Holic, **Yulin Li**, A. Lyndaker,* Cornell University

A sextant of Cornell Electron Storage Ring (CESR) is currently being upgraded with Double Bend Achromat (DBA) lattice and CHESS Compact Undulators (CCUs) in order to significantly boost the performance of Cornell High Energy Synchrotron Source (CHESS). With this upgrade, dubbed CHESS-U, CESR is converted from a counter-propagating two-beam ring to a single-beam ring, and the beam energy will be increased from 5.3 GeV to 6 GeV. The beam current for normal operation will also be increased, from 120 mA to 200 mA. The beampipe aperture of this new section is much smaller than the rest of CESR, and therefore the beam pipes and vacuum pumping are quite different from the rest of CESR too.

The beam pipes are mainly made of three types of aluminum extrusions, fitting inside quadrupole magnets, dipole magnets, and undulators respectively. The dipole extrusion includes an ante-chamber for distributed pumping using NEG strips (SAES St 707). An exception is the dipole chamber from which the undulator X-ray beam exits. This chamber is instead made of two machined halves that are welded together.

In this presentation, we will give a brief overview of the design of the vacuum system, and then show some important details in chamber production and installation, such as extrusion bending by stretch forming, chamber welding and distortions, NEG strip pumping, etc. Base vacuum performance will be reported as well. Details regarding the crotch absorber will be reported in a separate presentation.

9:20am **VT-TuM5 Design and Fabrication of CHESS-U Crotch Absorbers***, Y. Li, **Xianghong Liu**, A. Lyndaker, K. Smolenski, A. Woll, L. Smieska,* Cornell Laboratory of Accelerator-based Sciences and Education

A major upgrade project (CHESS-U) will elevate performance of Cornell High Energy Synchrotron Source (CHESS) to a state-of-the-art 3rd generation light source. In the CHESS-U project, ~80 meters of Cornell Electron Storage Ring (CESR) will be upgraded with a Double Bend Achromat (DBA) lattice and CHESS compact undulators (CCUs), together with new CHESS front-ends and X-ray beamlines. Tremendous progresses have been made in the design, construction, and test of all required new accelerator components (such as magnets, vacuum chambers, etc.), and we are on schedule for the CHESS-U installation in late 2018.

One of the most challenging vacuum components is the crotch absorbers at the synchrotron radiation (SR) exit ports at the ends of dipole bending chambers. CHESS-U is designed for 250-mA maximum beam current at 6-GeV beam energy. The crotches need to safely absorb 5.1 kW of SR power generated by the dipole magnets at small angles of incidence, while allowing the undulator beams produced by the canted CCUs to pass. We present a design for a compact crotch which can effectively dissipate this high SR power and will be compatible with the ultra-high vacuum system of CESR.

The crotch is a composite of a 5-mm thick beryllium outer ring, which acts as a SR diffuser, and an axially water cooled copper cylinder, similar to the existing CHESS crotches that have been in operation for decades. The outer beryllium ring is bonded to the copper cylinder via vacuum furnace braze using Cusiltin (60% Ag - 30% Cu - 10% Sn) braze alloy. Thermal analysis has shown no surface temperatures higher than 325°C. However, the calculated maximum thermal stress (on the surface of the beryllium) is near beryllium’s ultimate strength. As a practical validation of the CHESS-U crotch design, an existing CHESS crotch was removed from CESR for microscopic inspection. Though the CHESS crotch was exposed to slightly higher SR power (5.7 kW) during operations, no sign of fracture, surface melting, or other visible defect was detected on the beryllium surface. To ensure the good bonding of the beryllium diffuser ring to the copper cylinder, scanning X-ray fluorescence (XRF) inspections of the brazed crotches were performed at CHESS A1 beamline. The XRF inspection verified the presence of a continuous braze layer (corresponding to 10-30 µm thickness of Cusiltin) between the beryllium and the copper, indicating good braze joint. Five CHESS-U crotch assemblies have been successfully fabricated and XRF inspected, to fulfill the need for 4 crotches required for the CHESS-U project.

9:40am **VT-TuM6 Simulation and Measurement of the Tritium Retention in the Beamline of the KATRIN Experiment***, **Joachim Wolf**,* Karlsruhe Institute of Technology, Germany

The objective of the KATRIN neutrino experiment is the determination the effective mass of electron anti-neutrinos with an unprecedented sensitivity of 0.2 eV/c^2 by measuring the energy spectrum of b-electrons from tritium decays close to the endpoint of the spectrum. The decays take place in a high-intensity windowless gaseous tritium source (WGTS). The electrons are guided by strong magnetic fields through a beamline with super-conducting solenoids to the huge main spectrometer for energy measurement. Since only a fraction of $2 \cdot 10^{-13}$ of all electrons have a kinetic energy within 1 eV below the spectral endpoint, the sensitivity of the measurement depends on a low background rate in the spectrometer. Therefore the tritium flow from the source (10^{-3} mbar) has to be reduced by at least 14 orders of magnitude before it reaches the spectrometer section. This large reduction in the 90-mm-diameter beamline is achieved with a combination of a differential pumping section (DPS), using turbo-molecular pumps (TMP) and a cryogenic pumping section (CPS) with an argon frost layer at around 3 K.

This talk describes the Test Particle Monte Carlo (TPMC) simulation of the beamline for the differential and cryogenic pumping sections both for the non-radioactive gas deuterium and for tritium with MolFlow+. Since the gas flow through the CPS is reduced by far more than 7 orders of magnitude, the simulation is done in several consecutive steps. The results are combined in the post processing of the TPMC results. In the post processing algorithm we also investigate the time dependence of the reduction factor by considering a finite sojourn time of the molecules on the cryogenic argon layer. This leads to a slow migration of deuterium in downstream direction. In a final step the half-life and migration of tritium is taken into account by a reduced sojourn time.

After finishing the construction of the KATRIN setup, the final commissioning of the experiment started in October 2016. The results of the commissioning measurements with deuterium will be compared with the TMPC simulations. First traces of tritium are planned to be admitted into the beamline in May 2018. This work has been supported by the German BMBF (05A17VK2).

11:00am **VT-TuM10 NSLS-II Beamline Vacuum Challenges: Design, Commissioning, and Operations***, **Robert Todd**, C. Hetzel,* Brookhaven National Laboratory

The NSLS-II facility now has 23 beamlines in operation and 5 others nearing operational readiness. This talk will focus on general vacuum requirements common to all synchrotron beamlines as well as hardware and design considerations needed to meet them. Topics to be covered include: beamline vacuum system design, leak checking, bakeout, commissioning, and operation. Particular attention will be given to the successes and challenges experienced to date.

11:20am **VT-TuM11 Thin film Heterostructures for Superconducting Photocathode Applications***, **Mark Warren**,* Illinois Institute of Technology

In the application of high pulse rate (100 MHz) CW light sources, superconducting RF guns serve as ideal photoinjectors as they dissipate significantly less power than normal metal Cu. An integral component of a photoinjector, the photocathode, must produce an electron beam with stringent requirements on emittance, temporal response, and quantum efficiency (QE). The photoinjector wall material is most commonly Nb which itself has a low QE (10-6). So, it is proposed that Nb photocathodes be coated with thin films of Mg which have a much higher QE (0.1% with laser cleaning) and can be induced into the superconducting state via the proximity effect. Results on the fabrication and testing of Nb/Mg bilayers including the resiliency of thin films in high RF fields (up to 60 MV/m) will be presented. In addition, the study of semiconducting overlayers is presented including promising QE values in ultra-thin layers of Cs2Te on Nb.

11:40am **VT-TuM12 TPD Results on Electrode Materials for Pulsed Power Vacuum Environments***, **Ronald Goeke**, S.C. Simpson, K.R. Coombes, M.K. Alam, D.P. Adams,* Sandia National Laboratories

Next generation pulsed power systems require a better understanding of current loss and the ability to predict the scaling of current coupling. Plasma formation occurs in these devices at both the anode and cathode at high current densities. These plasmas are formed from desorbed and ionized surface and bulk electrode contaminants, expand into the anode-cathode gaps of the transmission lines (a phenomenon referred to as plasma closure), and potentially lead to shunting of current away from the fusion targets. Contaminants are pervasive on typically manufactured hardware and common on pulsed power vacuum systems. Understanding the physics of neutral desorption from electrode surfaces is a critical requirement for accurately predicting plasma formation (current loss) in pulsed power machines, We will present Temperature Programmed Desorption (TPD) results of common electrode materials, including machined wrought stainless steel and additively manufactured 304L stainless steel.

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Exhibitor Technology Spotlight Workshops
Room Hall A - Session EW-TuB

Exhibitor Technology Spotlight Session I

Moderator: Christopher Moffitt, Kratos Analytical Inc

10:20am **EW-TuB2 IMPULSE HIPIMS Power Supply with Positive Pulse Option Advantages*, Jason Hrebik,*** Kurt J. Lesker Company

HIPIMS is an ionized PVD technique that produces a high density, high performance films. The extreme power densities in HIPIMS create a higher ionized plasma that creates a very high energy of material being deposited onto the substrate.

The IMPULSE HIPIMS supply offers a cost effective solution for HIPIMS research and process development. The IMPULSE is a scalable option for higher power applications ideal for production application scale up.

The supplies broad range of parameter adjustment along with its positive kick pulse option, provide the tools necessary to tune each process for ideal performance. This presentation will share examples of applications and performance data to support the many advantages of the IMPULSE power supply. The available configurations and examples of ideal operating parameters will be shared.

10:40am **EW-TuB3 Choosing the Proper Equipment for Vacuum Heat Treatment*, Rachael Stene,*** Across International

Selecting the proper equipment is the first step in completing a successful process. There are several factors to consider such as target temperature, required heating rate to achieve a certain time to temperature, desired vacuum level, sample size, chemistry of the system's atmosphere, and more. Here, we elaborate on the many aspects which may be involved in your application, helping you select the perfect components for the operation. Across International’s line of material processing equipment offers several advantages and comes with many helpful features, which sets us apart. We’ll elaborate on these factors and the AI advantage in this presentation.

Manufacturing Science and Technology Group
Room 103C - Session MS-TuB

Working with Government Labs and other User Facilities

Moderator: Bridget Rogers, Vanderbilt University

10:00am **MS-TuB1 Joining the Research Community at the Cornell NanoScale Science and Technology Facility*, Michael Skvarla,*** Cornell University

The Cornell Nanoscale Science and Technology Facility (CNF) is one of network of open-access shared facilities partially subsidized by the US National Science Foundation to provide researchers with rapid, affordable, shared access to advanced nanofabrication tools and associated staff expertise. Projects can be accomplished either hands-on or remotely. Hundreds of engineers and scientists worldwide, from throughout academia, industry, and government, utilize CNF to make structures and systems from the nanometer scale to the centimeter scale. All users are welcome; no experience in nanofabrication is necessary and a central part of CNF’s mission is to assist users from “non-traditional” fields seeking assistance to implement nanofabrication techniques for the first time. CNF’s user program is designed to provide the most rapid possible access (as little as 2 weeks from first contact) with the lowest possible barriers to entry (users retain full control of their IP, with no entanglement by CNF or Cornell University). CNF offers unique capabilities in world-leading electron-beam lithography, advanced stepper photolithography, dedicated facilities for soft lithography, and direct-write tools for rapid prototype development, along with the flexibility to accommodate diverse projects through the ability to deposit, grow, and etch a wide variety of materials. CNF’s technical staff is dedicated full-time to user support, providing one-on-one help with process development, tool training, and troubleshooting. They can offer expertise for a wide range of fabrication projects, including electronics, nanophotonics, magnetics, MEMS, thermal and energy systems, electrochemical devices, fluidics, and basic studies in physics, chemistry, and the life sciences (30% of CNF’s users now come from the biology/bioengineering fields). This talk will explore the tools, services, and advice available to CNF users, and present examples of ongoing work with the hope of stimulating ideas and possibilities. CNF is a member of the National Nanotechnology Coordinated Infrastructure (NNCI) program, a new NSF-sponsored network of shared facilities. We invite you to explore the CNF and NNCI, and discuss ways we can help bring your research visions to fruition. The CNF technical staff meets every Wednesday afternoon for conference calls where we welcome questions about any topic related to nanofabrication and can provide detailed processing advice and cost estimates for potential new projects. Visit cnf.cornell.edu to contact us and get started.

10:20am **MS-TuB2 Opportunities at DOE Nanoscale Science Research Centers*, Arthur Baddorf,*** Oak Ridge National Laboratory

DOE Nanoscale Science Research Centers (NSRCs) were established for use by the international science community to advance scientific and technical knowledge in nanoscale science. The mission of the NSRCs is twofold: to enable the external scientific community to carry out high-impact nanoscience projects through an open, peer-reviewed user program, and to conduct in-house research to discover, understand, and exploit functional nanomaterials. To fulfill this mission, the NSRCs house the most advanced facilities for nanoscience research and employ world-class scientists who are experts in nanoscience and enjoy working with external users. Access to these centers is through a simple, peer-reviewed proposal process and is free-of-charge if the user intends to publish the research results in open literature.

As an example, the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) provides access to expertise and equipment for a broad range of nanoscience research, including nanomaterials synthesis, nanofabrication, imaging/characterization, and theory/modeling/simulation. CNMS also acts as gateway for the nanoscience community to benefit from ORNL’s neutron sources and computational resources. In addition to a broad assortment of nanomaterials characterization tools, the CNMS has specific expertise in the following capabilities:

- Nanofabrication
- Bio-Inspired Nanomaterials
- Inorganic and Hybrid Nanomaterials Synthesis
- Macromolecular Nanomaterials Synthesis
- Chemical Imaging
- Electron and Atom Probe Microscopy
- Scanning Probe Microscopy
- Nanomaterials Theory

This talk will provide a broad overview of opportunities at NSRCs and how to take advantage of their capabilities and expertise through user programs. More information can be found at https://nsrcportal.sandia.gov/

Exhibitor Technology Spotlight Workshops
Room Hall A - Session EW-TuL

Exhibitor Technology Spotlight Session II
Moderator: Christopher Moffitt, Kratos Analytical Inc

12:40pm **EW-TuL3 Correlative Spectroscopy with the Thermo Scientific Nexsa*, Tim Nunney*, *P. Mack, R.E. Simpson,* Thermo Fisher Scientific, UK**

In this presentation we will highlight how the multi-technique capabilities of the Thermo Scientific Nexsa system can be used to analyse samples from a range of application areas.

1:00pm **EW-TuL4 Exploring the Capabilities of a Modern XPS Spectrometer: In-situ Surface Preparation & Modification*, Adam Roberts,*** Kratos Analytical Limited, UK*; D. Surman, C. Moffitt,* Kratos Analytical Inc*; J.D.P. Counsell,* Kratos Analytical Ltd, UK

XPS is unique in being able to generate quantitative, chemical state information from a wide range of conducting, semiconducting and insulating materials. The information can be extremely surface sensitive, probing the outermost 1 -3 nm of the surface by angle resolved XPS. Higher energy X-ray excitation sources, such as Ag Lα (2984.2 eV) can be used to generate information from the near surface, up to 20 nm, whilst the destructive sputter depth profiling using Ar_n^+ gas clusters can provide XPS data from several microns into the 'bulk' material.

These attributes of the modern spectrometer can be used in combination with in-situ modification of surface chemistry. Such an approach is of importance in gaining a better understanding of the functionality of materials. To aid research of these types of samples Kratos has developed a high pressure gas reaction cell allowing samples to be exposed to pressures up to 20 bar and temperatures of 1000 °C with static or dynamic gas flow conditions. The integrated gas handling system ensures that the samples can be processed for oxidation and reduction reactions dependent on the gases used. Use of this accessory is independent of the main analysis chamber with samples transferred from the gas reaction cell for analysis at normal UHV conditions. This approach ensures that the photoelectron transmission of the spectrometer remains constant and charge neutralisation is not compromised during the XPS analysis.

A further development for in-situ sample preparation is the integration of evaporation sources onto the AXIS spectrometers. The easy movement of samples through the spectrometer ensures that chemistry of thin-film deposition can be followed by XPS through the deposition cycles. It is also possible to compliment XPS measurements with low energy ion scattering spectroscopy (ISS), probing the outermost atomic layer of the sample and allowing the determination of film-closure for example.

This presentation will demonstrate the latest capabilities of the Kratos X-ray photoelectron spectrometers for lateral and depth distribution of elemental and chemical state through the characterisation of in-situ deposited and high temperature/pressure modified surfaces.

1:20pm **EW-TuL5 Design and Characterization of Nanomaterials using PREVAC's Research Platforms*, Lukasz Walczak,*** PREVAC sp. z o.o., Poland

Magnetics, optoelectronics, energy storage and renewables, catalysis and nanoelectronics, semiconductors, new graphene-type materials and their surface are under intensive investigation of many research groups [1-3]. The wide variety of novel technologies and materials available, precise, well defined scientific problems or proprietary production recipes demand customized analysis and deposition systems. Innovative and compact PREVAC surface analysis platform as part of multi-technique surface analysis system will be presented, in order to permit complete characterization of nanomaterials in the UHV and ambient pressure conditions. We will report some results from these systems. Also we introduced PREVAC deposition platforms, based on well tested MBE system technology, offering a high quality and stable UHV performance. Compact construction allows the connection of different deposition sources at versatile configurations as well as the incorporation of RHEED, inventive alternative GIFAD [4] and other analysis techniques. As the next deposition platform the sputtering systems for depositing metal and dielectric thin films on substrates at the different temperature will be shown. A range of magnetron sputtering sources, using RF, DC, or pulsed DC power, can be operated in the multimode by SYNTHESIUM software for producing thin films. Finally we describe PREVAC's PLD systems. Typically it is used with a focused pulsed excimer laser to vaporize a small section of a solid target material in a vacuum chamber in order to produce thin-films. Standalone configuration or as part of a larger integrated research system, system is fully automated. The transfer system features a six position target manipulator which allows transfer of both target and substrate holders for simple and efficient operation.

References:

1. L. K. Preethi, et al., Sci. Rep. 7, 14314 (2017)

2. M. Weis, et al., Sci. Rep. 7, 13782 (2017)

3. N. M. Freitag et al., Nature Nanotechn. 13, 392-397 (2018)

4. A. Momeni et al. J. Phys. Chem. Lett., 9, 908–913 (2018)

1:40pm **EW-TuL6 Agilent's New Helium Leak Detector*, John McLaren,*** Agilent

Earlier this year Agilent Technologies introduced its new Helium Leak Detector (HLD). Building on Agilent's leadership position in mass spectrometry, this new instrument sets the standard for ease of use and application-specific operation. Users can quickly navigate to one of six unique setup screens and be guided in setting the proper test parameters, achieving optimum performance and efficiency for their specific application. No more guessing, wasting time or making costly mistakes. A large 8.4 in. (21 cm) display features a completely revised user interface, with eight available languages, that is extremely intuitive and employs familiar icons and imagery simplifying training. Selectable security levels protect the integrity of the test while allowing access for operators, process engineers, and maintenance technicians. Agilent is the only helium leak detector manufacturer that designs and manufactures the entire instrument, mass spectrometer, high vacuum split-flow turbomolecular pump and rotary vane and dry scroll roughing pumps. The latter employing our patented dual pump design, delivering superior pumping speed and helium handling performance even in high background environments. Components are designed to work together and with everything Agilent-made and Agilent supported, users are secure in their investment. The HLD is available in 3 different form factors, both wet and dry primary pumps, each in three different sizes, allowing the most configurations in the industry. Unparalleled ease-of-use and application guidance makes the HLD the instrument of choice for any leak test. Our spotlight session will demonstrate how our application setups guide the user in correctly configuring their instrument for the best performance, establishing correct parameters for a thorough and efficient test. Each setup offers the following benefits:

- Display all relevant settings on one page. No need to navigate through multiple screens or struggle to recall which settings are needed.
- Save time in both setup and testing.
- Automatically incorporate certain settings as dictated by the application. No need to decipher every arcane detail in the manual and wonder what settings should be turned on or off.
- Provide on screen help and guide the user through the setup.

2:00pm **EW-TuL7 Auger Multi-Technique: EDS, EBSD, BSE, FIB*, John Newman,*** Physical Electronics

Auger Electron Spectroscopy (AES) is a very power surface sensitive technique used for determining the composition of micron and sub-micron sized features, as well as for general thin film analysis. Its application has found widespread use in various fields of study such as semiconductors, microelectronics, metallurgy, fracture analysis, corrosion, catalysis, thin film coatings, and failure analysis. While Auger by itself can solve many problems, at times, the combination of other techniques with Auger can provide complementary data useful for more complete characterization of materials. This presentation will describe PHI's 710 Multi-technique instrument with Auger, EDS, EBSD, BSE and FIB capabilities. Applications of each technique will be shown, demonstrating how the instrument can be used for advanced materials characterization.

2D Materials Focus Topic
Room 201B - Session 2D+EM+MI+MN+NS-TuA
2D Device Physics and Applications

Moderator: Roland Kawakami, The Ohio State University

2:20pm **2D+EM+MI+MN+NS-TuA1 Spin Relaxation and Proximity Effect in WS₂/Graphene/Fluorographene Non-local Spin Valves***, **Adam Friedman**,* Laboratory for Physical Sciences*; K.M. McCreary, J.T. Robinson, O.M.J. van 't Erve, B.T. Jonker,* US Naval Research Laboratory

The mechanisms leading to spin relaxation in graphene and its heterostructures continue to be debated. Control of the spin relaxation in graphene-based structures is necessary to achieve the envisioned utility of graphene in future spintronic devices beyond Moore's law. Proximity induced spin relaxation caused by contact to a high spin-orbit material, such as WS_2, offers a promising avenue to manipulate the spin lifetime [1]. We demonstrate the operation of WS_2/graphene/fluorographene non-local spin valves and extract the spin lifetimes for a range of carrier concentrations by Hanle effect measurements. Four-terminal charge transport measurements allow us to calculate the momentum relaxation time as a function of carrier concentration and compare it to the spin lifetime. These data show that the D'yakonov-Perel' mechanism is the dominant spin relaxation mechanism for WS_2/graphene/fluorographenedevices, while, for reference graphene/fluorographene devices, linear scaling between the spin and momentum lifetimes points to spin-flip scattering during strong elastic scattering events where the scattering event is strongly coupled to the electron spin. We attribute the change in spin relaxation type in part with the inclusion of WS_2 as a substrate to proximity induced spin-orbit coupling due to the adjacent WS_2 layer, and we compare our data to the literature.

[1] A.L. Friedman, et al. Carbon 131, 18-25 (2018).

2:40pm **2D+EM+MI+MN+NS-TuA2 Two-dimensional Field-effect Light Emitting Transistors***, **Junyoung Kwon**, H. Ryu,* Yonsei University, Republic of Korea*; J.Y. Lee, C.H. Lee,* Korea University, Republic of Korea*; G.H. Lee,* Yonsei University, Republic of Korea

Two dimensional (2D) materials and their heterostructures hold great promises in various applications due to their unique properties and newly discovered physics. Especially, high exciton binding energy and emergence of charged excitons, *i.e.* trions, have shown that 2D semiconductors, such as transition metal dichalcogenides (TMDs), are promising candidates for new concept optoelectronics. Although lots of optoelectronic devices based on the van der Waals heterostructures of 2D materials, such as photodetectors, solar cells, and light emitting devices, have been demonstrated, development of novel optoelectronic devices is still required to fully utilize unique properties of 2D materials and enable multi-functions and versatile applications. Here we demonstrate 2D filed-effect light emitting transistors (2D-FELET) consisting of monolayer WSe_2 (light-emitting channel layer) and graphene contacts (tunable carrier injection electrodes). We encapsulated monolayer WSe_2 with two pieces of hexagonal boron nitride and fabricated graphene contacts to two ends of WSe_2. To selectively inject different types of charge (electrons and holes) at two graphene contacts, two separate top gates on top of WSe_2-graphene overlap regions were fabricated. By independent modulation of two top gates, Schottky barrier heights for electrons and holes can be tuned, which enables the selective charge injections. When two top gates are oppositely biased, electrons can be injected from one end of WSe_2 channel and holes can be injected from the other end. These opposite charges are recombined at the middle of WSe_2 channel, leading to strong light emission. The performance of the 2D-FELETs is tunable by additional electrical field from back gate. Furthermore, the devices produced in this work can be used as polarity-tunable FETs and photodetectors, simultaneously, which are beneficial for further CMOS integration. Our study shows great potential of 2D-FELETs toward future optoelectronic applications, which request ultra-thinness, transparency, flexibility, high efficiency, multi-functions, and high integration.

3:00pm **2D+EM+MI+MN+NS-TuA3 Quantum Devices with 2D Materials***, H. Overweg, M. Eich, R. Pisoni, T. Ihn, P. Rickhaus,* ETH Zurich, Switzerland*;* ***Klaus Ensslin**,* ETH Zürich, Switzerland **INVITED**

Quantum dots in graphene have been mostly realized by etching. This leads to localized states at the uncontrolled edges dominating the transport properties of these quantum devices. [1] It is well known that in bilayer graphene gaps can be opened by vertical electrical fields. [2] This approach has been used with limited success to define quantum devices [3]. The pinch-off characteristics are typically limited by leakage currents often thought to occur at the physical sample edges [4].

Here we demonstrate that electrostatically tunable barriers can be fabricated on bilayer graphene devices with graphite as a back gate. We measure pinch-off resistances exceeding GOhms and observe quantized conduction plateaus for one-dimensional constrictions. [5] With suitable gate arrangements few carrier hole and electron quantum dots can be electrostatically defined. We measure the controlled occupation of quantum dots with single holes and electrons. Four-fold level bunching is observed in Coulomb blockade spectroscopy which is understood in terms of valley and spin states. Magnetic field dependence allows to investigate orbital and spin/valley degrees of freedom.

We further demonstrate quantum devices build on MoS2.

1. For a review see Bischoff et al., Applied Physics Reviews 2, 031301 (2015)
2. Oostinga et al., Nat. Materials 7, 151 (2007)
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4:20pm **2D+EM+MI+MN+NS-TuA7 GaN Microdisk Light-emitting Diode Display Fabricated on Graphene***, **Youngbin Tchoe**, K. Chung, K. Lee, M.S. Song, J.B. Park, H. Kim, J.Y. Park, G.-C. Yi,* Seoul National University, Republic of Korea

Microdisplay with high resolution, brightness, and efficiency with long-term stability and reliability are highly required for advanced display technologies. Inorganic semiconductors LEDs best suits this purpose because they can emit very high density of light from a small area and they have very high efficiency and long-term stability. To use inorganic LEDs for display applications, various lift-off and transfer techniques of inorganic thin films grown on single crystal substrates, such as sapphire or Si, were developed. However, achieving display devices using inorganic semiconductor thin films is still very challenging because of the limited size and high manufacturing cost of the single crystal substrates, as well as the complicated processes required for lift-off and assembly. To resolve this problem, growths of inorganic semiconductor nanostructures and thin films on graphene substrates have recently been proposed, since graphene has great scalability and extremely thin layered hexagonal lattice structure as an excellent substrate for GaN growth. Moreover, the inorganic semiconductors prepared on large-area graphene can be transferred easily to or grown on elastic substrates to meet the flexibility demand. Here, we suggest a method of fabricating ultrathin, high-resolution inorganic microdisplay based on individually addressable GaN microdisk LED arrays grown on graphene dots.

Here, we report on the fabrication and EL characteristics of ultrathin and individually addressable GaN microdisk LED arrays grown on graphene dots for microdisplay applications. GaN microdisks were prepared by epitaxial lateral overgrowth on patterned graphene microdots on SiO_2/Si substrates using MOVPE. After preparing the GaN microdisk arrays, *p*-GaN and InGaN/GaN multiple quantum well, and *n*-GaN layers were heteroepitaxially grown on the surface of the GaN microdisks. Ultrathin layers composed of GaN microdisk LED arrays on graphene dot were prepared by coating a polyimide layer and lifting-off the entire layers from the substrate. Then, single-walled carbon nanotubes (SWCNTs)/Ni/Au and SWCNTs/Ti/Au multiple electrode lines were formed on the top and bottom surface of GaN microdisk arrays in an aligned manner and crossing each other. The electrical and optical characteristics of the individually addressable GaN microdisk array on graphene dots were investigated by measuring their *I–V* curves and EL characteristics at various bending conditions. We also confirmed that the ultrathin micro-LED display worked reliably under flexible conditions and continuous operation mode.

4:40pm **2D+EM+MI+MN+NS-TuA8 Room Temperature Magnetron Sputtering and Laser Annealing of Ultrathin MoS₂ for Transistor Device Fabrication on Flexible Polymer Substrates***, **Benjamin Sirota**,* University of North Texas*; N.R. Glavin,* Air Force Research Laboratory*; C. Arnold, A.A. Voevodin,* University of North Texas

Pulsed magnetron sputtering and subsequent laser annealing provide technologically attractive scalable route for producing two-dimensional (2D) semiconducting grade MoS_2 materials directly on the surface of flexible polymer substrates. In this study the room temperature magnetron sputtering was used to deposit 10 nm thick, amorphous MoS_2 films on flexible PDMS as well as rigid SiO_2/Si substrates. This was followed by 248 nm pulsed laser annealing to produce polycrystalline 2H-MoS_2 over large areas. Raman and XPS analysis confirmed that pulsed laser annealing with about 1 mJ/cm^2 energy density had induced film crystallization from amorphous to hexagonal, while preserving MoS_2 chemical composition, and avoiding formation of oxide phases or damage to the temperature-sensitive polymer surface. Electrical measurements confirmed an order of magnitude improvement in electrical conductivity of the laser annealed films as compared to amorphous MoS_2. Top-gated field effect transistor (FET) devices with laser annealed sputter grown MoS_2 were directly fabricated on PDMS surfaces. Oxygen substitution of sulfur in sputter deposited MoS_2 and polycrystallinity of the laser annealed 2H-MoS_2 films resulted in low mobility values when compared to mechanically exfoliated and chemical vapor deposition grown single-crystal 2D MoS_2. However, the described approach is intrinsically scalable and provides a direct growth route for the fabrication of 2D transition metal dichalcogenide semiconducting devices on the surface of flexile and stretchable polymers.

5:00pm **2D+EM+MI+MN+NS-TuA9 Black Phosphorus: Fundamental Properties and Emerging Applications***, **Han Wang**,* University of Southern California **INVITED**

In this talk, I will discuss our recent work in developing novel electronic and photonic devices based on the anisotropic properties of black phosphorus (BP) and its isoelectronic materials such as the monochalcogenides of Group IV elements. High mobility, narrow gap BP thin film (0.3 eV in bulk) fill the energy space between zero-gap graphene and large-gap TMDCs, making it a promising material for mid-infrared and long wavelength infrared optoelectronics. Most importantly, its anisotropic nature within the plane of the layers allow for the realization of conceptually new electronic and photonic devices. Here, I will first present our work in understanding the fundamental electronic and optical properties of black phosphorus using a newly developed scanning ultrafast electron microscopy (SUEM) technique and photoluminescence spectroscopy. Our recent the study of bandgap tuning in BP and the demonstration of a polarization sensitive BP mid-IR detector will then be presented. In the second half of my talk, I will discuss our work on developing two dimensional materials based artificial synaptic devices for neuromorphic electronics, including emulating the heterogeneity in synaptic connections using the anisotropic properties of BP and a tunable memristive device as a reconfigurable synapse. I will conclude with remarks on promising future research directions of low-symmetry electronics based on anisotropic 2D materials and how their novel properties is expected to benefit the next-generation electronics and photonics technologies.

5:40pm **2D+EM+MI+MN+NS-TuA11 Patterned Growth of Hybrid Bulk-2D Tungsten Diselenide for Transistor Applications***, **Quinten Yurek**, I. Liao, D. Barroso, A.E. Nguyen, N. Duong, G. Stecklein, L. Bartels,* University of California, Riverside

As device dimensions shrink, surfaces and interfaces between materials make up a larger volume fraction of a device leading to degrading device properties in 3D materials. One solution is to use 2D materials, however these materials introduce additional challenges. For instance, high resistance Schottky barriers and a small number of free charge carriers in comparison to bulk materials. The effective mobility of field effect transistors (FETs) based on two-dimensional (2D) single-layer transition metal dichalcogenide (TMD) films is frequently limited by barriers at the contacts, as opposed to the native properties of the TMD material. Specifically, high resistance Schottky barriers form at the TMD/metal interface because of the film's thinness and resulting small number of carriers. Here we demonstrate a scalable single-step deposition method for nanoscale hybrid 2D/3D TMD structures encoded by lithographic patterning prior to deposition. By confining the metal contact to the bulk regions of WSe_2, the effective mobility is increased to nearly 100 cm^{2}V^{-1}s^{-1} with an on/off ratio >10^5 for bottom-gated devices (through 300nm of oxide), even for comparatively long channels (>5 microns) and absent other contact optimization. Our process involves lithographic patterning of a hafnium (IV) dioxide film onto the SiO_2/Si substrate prior to TMD growth. Bulk-like 3D WSe_2 is observed to grow at the location of the hafnia, while 2D single-layer material is grown in regions of bare SiO_2. Systematic evaluation of transport data allows us to extract Schottky barrier heights and other fundamental properties of our hybrid devices. We demonstrate that this process can be used to create devices with metal/3D TMD contacts, which exhibit a reduced Schottky barrier height, while continuing to use 2D TMD channels, which result in an excellent on-off ratio.

6:00pm **2D+EM+MI+MN+NS-TuA12 Enhanced Ionic Sensitivity in Solution-Gated Graphene-Hexagonal Boron Nitride Heterostructure Field-Effect Transistors***, A.D. Radadia, **Nowzesh Hasan**, B. Hou, A.L. Moore,* Louisiana Tech University

The charge transport in solution-gated graphene devices is affected by the impurities and disorder of the underlying dielectric interface and its interaction with the solution. This paper reports advancement in field-effect ion sensing by fabricating a dielectric isomorph, hexagonal boron nitride between graphene and silicon dioxide of a solution-gated graphene field effect transistor. Ionic sensitivity of Dirac voltage as high as -198 mV/decade for K$^+$ and -110 mV/decade for Ca^{2+} were recorded. Increased transconductance due to increased charge carrier mobility was accompanied with larger ionic sensitivity of the transconductance due to larger ionic sensitivity of the charge carrier mobility. These findings define a standard to construct future graphene devices for biosensing and bioelectronics applications.

Applied Surface Science Division
Room 204 - Session AS-TuA

The Impact of Modeling (Ion, Electron) and Data Analysis on Applied Surface Science, a Celebration of the Career of Barbara Garrison

Moderators: Gregory L. Fisher, Physical Electronics, Alexander Shard, National Physical Laboratory, UK

2:20pm **AS-TuA1 Collective Action, the Key to Soft Molecule Desorption under Particle Bombardment***, **Arnaud Delcorte**,* Université catholique de Louvain, Belgium **INVITED**

The focus of this contribution is on desorption of large non-volatile organic molecules induced by ion beams, for 2D and 3D analysis by secondary ion mass spectrometry (SIMS). It is also the story of my long-term collaboration with Pr. Barbara Garrison since 1999, when I started my post-doc under her guidance. Our first molecular dynamics (MD) simulations of polystyrene emission from silver induced by atomic projectiles gave us direction: in order to emit large molecules with minimal internal energy, collective action of the substrate atoms was required, which only occurred in so-called high (sputter) yield events where most of the projectile energy was deposited in the extreme surface [1]. These high yield events, rare with atomic ions, happened to be the rule with cluster projectiles such as C_{60}, where the collision cascades fully overlapped [2]. The use of C_{60} therefore led to remarkable sputtering yield enhancements for organic samples, and much improved emission of molecular ions in SIMS [3]. Clusters were the solution. We then naturally moved to larger clusters, where the physics shifted again, to macroscopic-like impacts phenomena [4]. Our simulations using large organic and argon clusters showed similar trends and, in particular, they quantitatively predicted the experimental 'universal' sputtering curves for the Ar cluster bombardment of organics [5]. The simulations also uncovered a region of energy, scaled by the number of atoms in the projectile (E/n), where fragmentation was minimized and intact molecular emission, maximized. All of this could not have been achieved without the great collective spirit and action that were maintained by Pr. Garrison in her 'extended team' over the years.

[1] A. Delcorte and B. J. Garrison, *High Yield Events of Molecular Emission Induced by Kiloelectronvolt Particle Bombardment*, J. Phys. Chem. B2000, *104,* 6785.

[2] A. Delcorte and B. J. Garrison, *Sputtering Polymers with Buckminsterfullerene Projectiles: A Coarse-Grain Molecular Dynamics Study*, J. Phys. Chem. C2007, *111,* 15312.

[3] D. Weibel, S. Wong, N. Lockyer, P. Blenkinsopp, R. Hill, J. C. Vickerman, *A C60 Primary Ion Beam System for Time of Flight Secondary Ion Mass Spectrometry: Its Development and Secondary Ion Yield Characteristics*, Anal. Chem. 2003, 75, 1754.

[4] A. Delcorte, B. J. Garrison, K. Hamraoui, *Dynamics of Molecular Impacts on Soft Materials: From Fullerenes to Organic Nanodrops*, Anal. Chem.2009, *81,* 6676.

[5] A. Delcorte and M. Debongnie, *Macromolecular Sample Sputtering by Large Ar and CH4 Clusters: Elucidating Chain Size and Projectile Effects with Molecular Dynamics,* J. Phys. Chem. C 2015, 119, 25868.

3:00pm **AS-TuA3 Mechanisms of the Generation of Nanoparticles and Surface Modification in Short Pulse Laser Ablation of Metal Targets in Liquids***, **Leonid Zhigilei**, C.-Y. Shih, M. Shugaev,* University of Virginia

The ability of short pulse laser ablation in liquids to produce clean colloidal nanoparticles and unusual surface morphology has been employed in a broad range of practical applications. In this presentation, the results of large-scale molecular dynamics simulations aimed at revealing the key processes that control the surface morphology and nanoparticle size distributions generated by pulsed laser ablation in liquids [1-4]. The simulations of Ag and Cr targets irradiated in water are performed with an advanced computational model combining a coarse-grained representation of liquid environment and an atomistic description of laser interaction with metal targets. One of the interesting predictions of simulations performed at sufficiently high laser fluences, in the regime of phase explosion, is the emergence of Rayleigh–Taylor and Richtmyer–Meshkov hydrodynamic instabilities at the interface between ablation plume and superheated water, leading to the formation of nanojets and emission of large droplets into the water environment. The droplets are rapidly quenched and solidified into nanoparticles featuring complex microstructure and metastable phases, as demonstrated by example structures shown in the middle of the cover. Rapid nucleation and growth of small nanoparticles in the silver–water mixing region and the breakup of the hot metal layer into larger droplets due to the hydrodynamic instabilities represent two distinct mechanisms of the nanoparticle formation that yield nanoparticles of two different size ranges as early as several nanoseconds after the laser irradiation. This computational prediction provides a plausible explanation for experimental observations of bimodal nanoparticle size distributions in short pulse laser ablation experiments.

[1] **C.-Y. Shih *et al.*, J. Colloid Interface Sci. 489, 3-17, 2017**.

[2] M. V. Shugaev *et al.*, Appl. Surf. Sci. **417**, 54-63, 2017.

[3] C.-Y. Shih *et al.*, J. Phys. Chem. C **121**, 16549-16567, 2017.

[4] C.-Y. Shih *et al.*, Nanoscale **10**, 6900-6910, 2018.

3:20pm **AS-TuA4 First Principles Thermodynamics and Molecular Modeling of Surfaces in Aqueous Environments***, **Donald Brenner**, Z. Rak, L. Su, J. Krim,* North Carolina State University

We have been using first-principles thermodynamics and molecular modeling to characterize the structure, stability and dynamics of solid surfaces in aqueous environments. This talk will focus on two recent examples from our research. The first involves understanding and predicting the thermodynamics of the corrosion of stainless steel and nickel alloys in contact with the coolant in nuclear pressurized water reactors, as well as the driving force that leads to unwanted deposits on the fuel rod cladding from the corrosion products. The second example is a molecular modeling study of the adhesion of functionalized nano-diamond clusters to a gold substrate. Our simulations have revealed a new phenomenon, a molecular water layer containing solvated counter ions between a gold substrate and a negative nano-diamond that is facilitated by surface functionalization, and that is not present for a positively charged nano-diamond. The resulting electro-static screening leads to a weaker adhesion of negative nano-diamonds compared to positive nano-diamonds, an effect that has been observed in prior experiments but not understood.

This work was supported by the Consortium for Advanced Simulation of Light-Water Reactors, a DoE Energy Hub, and by the National Science Foundation through grant DMR-1535082.

4:20pm **AS-TuA7 Computer Modeling of Cluster Projectile Impacts for SIMS Applications***, **Zbigniew Postawa**,* Jagiellonian University, Krakow, Poland **INVITED**

A few years ago, Secondary Ion Mass Spectrometry (SIMS) has celebrated its centennial. The first observation of secondary ions is credited to J.J. Thompson at the beginning of the twentieth century [1]. However, the golden era of SIMS began in the fifties and continues to this day. This period is associated with a plethora of ground-breaking equipment developments, experimental observations and theoretical explanations. Initially, theoretical descriptions were based on analytical models. However, soon it has been realized that a proper description of phenomena taking place in more complex materials goes beyond the capability of this treatment. The appearance of computers and computer simulations have breathed new life into the field [2]. Today, computer simulations are a vital counterpart to the experimental measurements due to the atomic resolution and ability to visualize processes taking place inside investigated solids. As ion beams have developed from argon, through gallium, gold, bismuth to metal clusters, C_{60} and now giant atomic and molecular clusters and as computers have become ever more powerful, analysis and simulation of ever more realistic materials has gone forward hand in hand. Barbara Garrison has been always at the forefront of all these endeavors.

In this talk, a few examples of theoretical studies, which Barbara has guided and/or inspired, will be given. Examples include efforts to understand a difference in processes stimulated by impacts of atomic and cluster projectiles [3], evolution of surface roughness during cluster bombardment and its influence on the depth resolution in depth profiling [4], and processes of molecular emission from cluster-bombarded novel ultra-thin graphene-based substrates used recently to enhance molecular ionization [5].

[1] J.J. Thompson, Rays of Positive Electricity, Philos. Mag. 20 (1910) 752.

[2] B.J. Garrison and Z. Postawa, *Molecular Dynamics Simulations, the Theoretical Partner to dynamic cluster SIMS Experiments*, in *ToF-SIMS - Surface Analysis by Mass Spectrometry - 2nd Edition*, Eds. D. Briggs and J. Vickerman (SurfaceSpectra Ltd/IM Publications, 2013) *and reference therein*.

[3] Z. Postawa, B. Czerwinski, M. Szewczyk, E. J. Smiley, N. Winograd and B. J. Garrison, *Microscopic Insights into the Sputtering of Ag{111} Induced by C_{60} and Ga Bombardment of Ag{111}*, J. Phys. Chem. B 108 (2004) 7831.

[4] D. Maciazek, R. Paruch, Z. Postawa, B.J Garrison, Micro- and Macroscopic Modeling of Sputter Depth Profiling, J. Phys. Chem. C 120 (2016) 25473.

[5] S. Verkhoturov, M. Gołuński, D. Verkhoturov, S. Geng, Z. Postawa, and E. Schweikert, Trampoline, J. Chem. Phys. **148** (2018) 144309.

5:00pm **AS-TuA9 Use of Ion-Solid Interactions Modeling and Theory for Real Applications in FIB Milling***, **Lucille Giannuzzi**,* L.A. Giannuzzi & Associates LLC

Many FIB techniques in sample preparation and prototyping have been developed with a knowledge and use of ion-solid interactions modeling and theory. Understanding ion-solid interactions at different incident angle, ion energy, dose, and effect of target crystallography, are crucial for quality FIB milling of materials [1,2]. A discussion on the modeling and theory of ion-solid interactions and its direct influence on FIB milling quality and results will be presented.

[1]Lucille A. Giannuzzi, Remco Geurts, and Jan Ringnalda,Microsc Microanal 11(Suppl 2), 828-829, 2005

[2]Michael F. Russo, Jr., Mostafa Maazouz, Lucille A. Giannuzzi, Clive Chandler, Mark Utlaut, and Barbara J. Garrison, Microsc. Microanal. 14, 315–320, 2008

5:20pm **AS-TuA10 The Influence of the Projectile Cluster on the Molecular Ionization Probability in SIMS***, **Lars Breuer**, A. Wucher,* Universität Duisburg-Essen, Germany*; N. Winograd,* The Pennsylvania State University

The implementation of cluster ion sources in secondary ion mass spectrometry (SIMS) opened the field to molecular imaging and depth profiling of organic materials. In the last years the trend to larger projectiles continued and led to gas cluster ion beams (GCIB) with projectiles consisting of thousands of atoms. The use of these projectiles not only reduces the chemical damage produced by the projectile impact and therefor preserves the molecular information, but also significantly increases the sputter yield of organic material. For the measured signal in a ToF-SIMS experiment the secondary ion yield is of greater interest. Here describes the probability that an intact quasi-molecular ion of species *i* is formed during the sputtering process. As for inorganics especially metals a long list of values for ionization probabilities has been reported in the literature only very little is known about ionization probabilities of organic molecules in particular under GCIB bombardment.

The knowledge of ionization probabilities and sputter yields is of great general importance. Not only is the process of ion formation not fully understood yet, but also can manipulating the ionization probability increase the sensitivity of the experiment. Possible approaches for such manipulations are changes is projectile size, kinetic energy and chemistry. The important question here is: “How much headroom is left to produce more secondary ions?”

To answer this question a measurement of the ion fraction in the flux of sputtered material is necessary. Such a measurement requires the direct comparison of the sputtered intact secondary (quasi-) molecular ion and its neutral counterparts. To perform such a measurement post-ionization without severe photo-fragmentation has to be performed. In our measurements we used a strong-field post-ionization scheme due to its universality and low fragmentation. In the past our lab performed this kind of measurements on material sputtered under C_{60} bombardment [1,2] which has been extended to the bombardment with GCIB in this study. As a result, we will compare ionization probabilities of sputtered molecular species under GCIB and C_{60} bombardment.

[1] Popczun, N.J., Breuer, L., Wucher, A. and Winograd, N., J. Am. Soc. Mass Spectrom. (2017) 28: 1182.

[2] Popczun, N.J., Breuer, L., Wucher, A. and Winograd, N., J. Phys. Chem. C 2017 121 (16), 8931-8937.

5:40pm **AS-TuA11 In Situ Liquid SIMS, a Molecular Eye for Examination of Liquids and Liquid Interfaces***, **Zihua Zhu**[1], Y. Zhang,* Pacific Northwest National Laboratory **INVITED**

Secondary ion mass spectrometry (SIMS) has proven to be a powerful surface analysis tool, because it can provide elemental, isotopic and molecular information with excellent sensitivity and decent spatial resolution. However, SIMS is a high vacuum technique, and it normally is used to analyze solid samples. In recent years, in situ liquid SIMS was developed in my lab with collaboration with Dr. Xiao-Ying Yu, allowing molecular examination of various liquids and liquid interfaces. In brief, an interesting liquid can be sealed within a vacuum compatible device, and a thin silicon nitride (SiN) membrane is used to separate the liquid from vacuum. Then, we use a focused primary ion beam to drill an aperture through the SiN membrane to expose the liquid for SIMS examination. The key design of this idea is the diameter of the aperture: if the diameter is less than 2-3 microns, surface tension of the liquid can hold the liquid without any spraying out. Also, the evaporation from the aperture is controllable, making SIMS measurements fully feasible. If using a cluster primary ion beam, molecular signals from liquid surfaces and solid-liquid interfaces can be readily collected. In situ liquid SIMS has been used to investigate electrode-electrolyte interfaces during electrochemical or electro-catalytic reactions. The uniqueness of this novel approach is simultaneous collection of molecular evolution information of electrode surfaces, reactants, intermediates, and products under operando conditions, offering the possibility to elucidate complicated chemistries occurring at electrode-electrolyte interfaces (e.g., solid-electrolyte interphase in lithium ion batteries). More interestingly, the ionization process of in situ liquid SIMS may be softer than regular electrospray ionization, which is surprisingly different from the traditional opinion that SIMS ionization process is very hard with strong damage. This new finding will shed light on molecular investigation of ion solvation, nucleation before nanoparticle formation, and similar complex processes occurring in liquid environments.

Biomaterial Interfaces Division
Room 101B - Session BI+AS+IPF+NS-TuA

IoT Session: Biofabrication, Bioanalytics, Biosensors and Diagnostics and Flash Networking Session

Moderators: Graham Leggett, University of Sheffield, UK, Tobias Weidner, Aarhus University, Denmark

2:20pm **BI+AS+IPF+NS-TuA1 Functionalization of Silica Materials *via* Click Reaction of Surface Silanol Groups with Vinyl Sulfones***, **Fang Cheng**, H. Wang, W. He, B. Sun, J. Qu,* Dalian University of Technology, China

Silica-based materials are widely used in the fields of catalysis, chromatography, biomaterials, biosensing and drug delivery due to their earth abundance and low cost. Success of these applications mostly relies on the functionalization of silica surfaces, among which covalent binding of organic molecules is preferred. Common strategies for the covalent functionalization of silica materials involve either silane treatments or Si-H reactions. Each has its share of limitations, with the former suffering from self-polymerization and multilayer modifications, and the latter being sensitive to moisture and oxygen. Herein, we proposed the 'click' reaction of silanol groups with vinyl sulfones, which enables a new and simple strategy for functionalization of silica materials. For the first time, the 'click' concept was extended to silanol groups that are abundant on the surface of silica materials, using compounds bearing vinyl sulfone groups. By simply immersing silica materials in vinyl sulfone solutions at 60℃, functionalization could be achieved in hours in the presence of catalysts. The chemical stability of vinyl sulfones and mild reaction conditions make this strategy advantageous than silane treatments and Si-H reactions. We demonstrated that silica materials with sizes ranging from microscale to macroscale could all be functionalized. Using compounds bearing multiple vinyl sulfone groups, silica materials can be further functionalized with varies of biomolecules due to the versatile reactivity of vinyl sulfone group towards thiol, amino and alcohols. Furthermore, the stability of resulting Si-O-C bond can be tuned by the properties of the vinyl sulfone compounds (e.g., hydrophobicity and surface density) as well as the environmental factors (e.g., solvents, pH and temperature). Increase in the hydrophobicity and functionalization density of the vinyl sulfone compounds could increase the stability of Si-O-C bonds. Contrast to the high stability in organic solvents, degradation of Si-O-C bond can be realized in aqueous solutions, which can be accelerated by addition of acid or base. This is rarely observed with bonds produced based of silane treatments and Si-H reactions. It could broaden the biomedical applications of functionalized silica, for example, to provide tailored release of drugs or proteins from silica surface.

2:40pm **BI+AS+IPF+NS-TuA2 Organosilica pH Nanosensors Applied to Realtime Metabolite Monitoring***, **Kye Robinson**,* Monash University, Australia*; K. Thurecht,* University of Queensland, Australia*; S. Corrie,* Monash University, Australia

Continuous monitoring of biomarkers in biological environments is a key challenge for the development of biosensors capable of providing real-time feedback[1]. These sensors promise to aid in the treatment of diseases with a highly dynamic nature however current technologies remain scarce[1]. Nanoparticle based "optodes" have emerged as sensitive and tuneable biosensors, using chromo/ionophores to generate analyte-specific changes in fluorescence spectra in a dynamic and reversible manner. Currently this type of sensor suffers from limitations including leaching of reagents from the nanoparticles over time, combined with poor colloidal stability and resistance to fouling in biological fluids.

An organosilica core-shell pH sensitive nanoparticle containing a mixture of covalently incorporated pH-sensitive (shell) and pH-insensitive (core) fluorescent dyes has been developed. This platform demonstrates good long term stability (80 days), fast response time (<100 ms) and resistance to fouling in biological conditions[2]. This presentation will describe the modification of these pH sensing particles towards the production of a lactate responsive particle for sensing through coupling with lactate dehydrogenase. Here we will present our latest results focussed on enzyme encapsulation in addition to modulation of shell parameters including thickness and degree of crosslinking in order to tune response kinetics for application in biological tissues.

[1] Corrie, S. R. et al., Analyst, **2015**, 140, 4350-4364

[2] Robinson, K. J. et al., ACS Sensors, **2018**

3:00pm **BI+AS+IPF+NS-TuA3 Impact of Different Receptor Binding Modes on Surface Morphology and Electrochemical Properties of PNA-based Sensing Platforms***, **Johannes Daniel Bartl**,* Walter Schottky Institut (WSI) and Physics Department, Technische Universität München, Germany*; P. Scarbolo,* Dipartimento Politecnico di Ingegneria e Architettura (DPIA), Università degli Studi di Udine, Italy*; S. Gremmo, G. Rziga, M. Stutzmann,* Walter Schottky Institut (WSI) and Physics Department, Technische Universität München, Germany*; M. Tornow,* Molecular Electronics Group and Department of Electrical and Computer Engineering, Technische Universität München, Germany*; L. Selmi,* Dipartimento di Ingegneria "Enzo Ferrari" (DIEF), Università di Modena e Reggio Emilia, Italy*; A. Cattani-Scholz,* Walter Schottky Institut (WSI) and Physics Department, Technische Universität München, Germany

Silicon-based field-effect devices have been widely studied for label-free DNA detection in recent years. These devices rely on the detection of changes in the electrical surface potential during the DNA recognition event and thus require a reliable and selective immobilization of charged biomolecules on the device surface [1]. The preparation of self-assembled monolayers of phosphonic acids (SAMPs) on metal oxide surfaces is an efficient approach to generate well-defined organic interfaces with a high density of receptor binding sites close to the sensing surface [2,3]. In this work, we report the functionalization and characterization of silicon/silicon nitride surfaces with different types of peptide nucleic acid (PNA), a synthetic analogue to DNA [4].

Differently modified PNA molecules are covalently immobilized on the underlying SAMPs either in a multidentate or monodentate fashion to investigate the effect of different binding modes on receptor density and morphology important for PNA-DNA hybridization. Multidentate immobilization of the bioreceptors *via* C_6-SH attachment groups at the γ-

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[1] **ASSD Peter Sherwood Award**

points along the PNA backbone provides a rigid, lying configuration on the device surface (PNA 1), whereas a monodentate immobilization by Cys-capped PNA molecules (PNA 2) results in more flexible and more accessible receptor binding sites. Our results indicate that the presented functionalization scheme can be successfully applied to produce morphologically and electrochemically different PNA bioreceptor binding sites on silicon/silicon nitride surfaces. Consequently, a well-chosen modification of the PNA backbone is a valid approach to influence the sensing properties of surface-immobilized PNA bioreceptors, which might provide an additional parameter to further tune and tailor the sensing capabilities of PNA-based biosensing devices.

[1] Ingebrandt S. and Offenhausser A., *Phys. Status Solidi A* **203** (2006), 3399–3411.

[2] Chaki N. K. and Vijayamohanan K., *Biosens. & Bioelectron*. **17** (2002), 112.

[3] Stutzmann M., Garrido J. A., Eickhoff M. and Brandt M. S., *Phys. Status Solidi A* **203** (2006), 3424–3437.

[4] Nielsen P. E. and Egholm M. (ed.), Peptide Nucleic Acids, Horizon Scientific Press (1999).

3:20pm **BI+AS+IPF+NS-TuA4 Biosensor for Detection of Gasotransmitter from Living Cells Employing Silver Nanorods Array**, ***Shashank Gahlaut**, C. Sharan, J.P. Singh,* Indian Institute of Technology Delhi, India

The detection of endogenous gases including H_2S is of immense interest nowadays as it opens the way to predict some diseases as well as an early stage diagnosis. These three gasotransmitter (H_2S, NO and CO) gaseous molecules transfer the information and give the signal for mainly cardiovascular diseases Therefore, its detection has crucial importance in bio-medical science. Here, we demonstrate H_2S detection from living cells using silver nanorods arrays fabricated by glancing angle deposition method. Colorimetric and wettability properties of silver nanorods are being observed for the gaseous detection. We use the model organism *E.coli* to demonstrate the feasibility of the method for the determination of live and resistant strains of the bacteria. For the human cell, we have used Hela cell line for the same. For the simplicity and feasibility of the technique, Android based mobile app has been developed for the colorimetric detection. Data obtained in this study show the potency of the system to identify live/dead bacteria with or without antibiotic treatment and compared with the time-consuming standard plating method, it a simple and cost-effective method for the estimation of living and resistant microorganism. The performance of AgNRs as H_2S gas sensor is investigated by its sensing ability of 5 ppm of gas with an exposure time of only 30 s. It has potential application in the area of antimicrobial resistance and bio-medical healthcare.

4:40pm **BI+AS+IPF+NS-TuA8 Polyzwitterion-modified Nanoparticles for Selective Antibody Separation**, *F. Cheng, C. Zhu,* ***Wei He**, B. Sun, J. Qu,* Dalian University of Technology, China

Antibody separation is a key biopharmaceutical process, which requires high specificity and efficiency in isolating the biomacromolecule from a complex biological fluid. Development of the separation adsorbent benefits diagnostics and therapeutics, such as point-of-care testing, treatment of cancer and autoimmune disease. In the process of antibody separation, Protein A chromatography is a commonly employed adsorbent, which could obtain antibody in high purity from serum or ascites. In the process-scale purification and therapeutic plasma exchange, safety issues, e.g. leakage and instability of the immobilized Protein A, and cross-contamination during regeneration, are overwhelmed in biopharmaceutics. An alternative approach to Protein A chromatography is using synthetic ligand, molecular weight of which is commonly less than 200 Da. The main advantages of synthetic ligand are well-controlled chemical structure, low cost, ease in clean-in-place, and repeatable regeneration capability in harsh conditions. However, it is a challenge to adsorb antibody in a highly selective manner from a complex biological fluid, which consists a variety of proteins with a broad range of concentrations.

Herein, we report a facile method to develop a quick separation adsorbent, which adsorbs antibody from a complex biological fluid with a high specificity. Two types of zwitterionic polymer-modified magnetic nanoparticles (NPs) are fabricated by conjugating pSBMA onto PEI-precoated NPs via either one-step method (1S NPs) or two-step method (2S NPs). For both methods, divinyl sulfone is used as linker molecule. Although 1S NPs were capable of resisting both IgG and BSA, 2S NPs exhibited specificity toward IgG adsorption in complex biological fluids, e.g. mixture of serums and IgG. The moderate interactions (Kd ~1.2 μM) between IgG and 2S NPs are three orders of magnitude lower than IgG binding with Protein A (Kd 10nM) . Through complementary characterizations and analyses, we rationalize that the surface developed herein with IgG specificity contains two key components: polyzwitterions with short chain length and sulfone groups with high density.

5:00pm **BI+AS+IPF+NS-TuA9 Orienting Proteins on Surfaces with Site-specific Bioorthgonal Ligations**, ***Riley Bednar**, R.A. Mehl,* Department of Biochemistry and Biophysics, Oregon State University

The functionalization of material surfaces with proteins is of great importance to a number of technologies, from industrial processes to biomedical diagnostics. However, while it has been proposed that orientation may be important to the function of such biomaterials, efforts to study such roles are hampered by a lack of rapid, quantitative, and orientation-specific immobilization techniques which will reduce non-specific fouling, and allow substoichiometric attachment of proteins onto surfaces in an orientation-controlled manner. Here, Carbonic Anydrase II (HCA)—a 30 kDA, monomeric metalloenzyme which catalyzes the interconversion of carbon dioxide to bicarbonate—is immobilized onto strained *trans*-cyclooctene (sTCO)-functionalized magnetic resin in an orientation-specific manner via bioorthogonal ligation with a site-specifically installed tetrazine-containing amino acid (Tet2.0).

5:20pm **BI+AS+IPF+NS-TuA10 High-throughput Study of the Role of Spatial Organization on the Activity of Surface-Bound Enzymes**, ***Nourin Alsharif**,* Boston University*; T. Lawton, J. Uzarski,* Natick Soldier Research, Development and Engineering Center*; K.A. Brown,* Boston University

Many of the exceptional properties of natural materials (e.g. fracture toughness of bones, strength to weight ratio of bamboo) can be attributed to their structural hierarchy, which originates, in part, from the nanoscale organization of the enzymes that synthesize these materials. In order to best utilize such enzymes *ex vivo* to grow engineered biomaterials, the role of this multiscale organization must be understood. Here, we report a novel strategy for studying the activity of arrangements of enzymes within a multifunctional material in a high throughput manner. In particular, we use top-down patterning techniques in conjunction with small molecule self-assembly to designate enzyme-binding regions amidst a non-binding, hydrophobic background. Key to this experimental scheme is the parallel nature of both the fabrication and the characterization processes that enable the efficient study of many geometric parameters of the enzyme-binding features. These parameters include, (1) feature size, (2) density of enzyme within each feature, and (3) distance between features. This level of control can in principle allow us to separate effects of reaction kinetics and substrate diffusion. Two strategies have been explored for the immobilization of enzymes including click chemistry to non-natural amino acids and binding to poly-histidine affinity tags. Top-down lithography and enzyme assembly were verified using a variety of surface characterization techniques including atomic force microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, spectroscopic ellipsometry, and contact angle goniometry. Initially, this high throughput paradigm is used to develop a fluorimetric assay to quantify the activity of surface-bound enzymes as a function of their spatial organization. Together with the widespread utilization of high throughput techniques in synthetic biology, the ability to study spatial organization in a rapid fashion is expected to dramatically improve *ex vivo* applications of enzymes.

5:40pm **BI+AS+IPF+NS-TuA11 Fabrication of Amino acid Contained Poly-lactic Acid Nanofibers by Electrospinning**, *C. Li,* National Yang Ming University, Taiwan, Republic of China*; J.H. Hsieh,* Ming Chi University of Technology, Taiwan, Republic of China*;* ***P.H. Lin**,* National Yang Ming University, Taiwan, Republic of China

Polylactic acid (PLA, $[C_3H_4O_2]_n$, CAS 26161-42-2) is a biodegradable and thermoplastic polymer. PLA is naturally produced and can be extracted from many plants such as sugarcane, cornstarch or cassava roots. Typical industrial production processes for PLA are direct condensation of lactic acid monomers (~100°C - 160°C) and ring-opening polymerization of lactide with metal catalysts. For applications in bulk forms, PLA can be produced by extrusion, casting, injection molding and spin coating or even 3d printing.

In cell and tissue engineering applications, amino acids are essential ingredients for cell-tissue culture, implants/replacements, drugs and treatment tests. There are twenty amino acids appearing in human genetic codes by triplet codons and usually categorized according to their polarity, acidity/basicity.

In this study, we fabricate nanofibers by electrospinning on a spin-coated PLA film. This specially designed combination of PLA films and nanofibers is meant to have enduring interfacial adhesion between the two for biomedical applications such as implants. Both PLA nanofibers and films are mixed with selected amino acids. Five amino acids were chosen: tryptophan (Trp,), methionine (Met,), serine (Ser,), glutamate (Glu,) and arginine (Arg,). The selection is based on the different electrical polarity of each amino acid. The electrical polarity has profound effects on the solubility, pH acidity of amino acids in water and many other associated biochemical functions. These amino acids are representatives of certain biochemical features for potentially different influences in our applications for cell culture.

The electrospinning process is controlled by several parameters such as the voltage of power supply, feeding velocity of polymer solution through the syringe pump, electrical field strength and distance to the collection plate of nanofibers. Different combinations of these parameters are studied to determine an optimal control for fiber formation. Properties of and microstructures of deposited films and nanofibers are investigated as following: thickness and deposition rate by surface profilometer; microstructures by Fourier transform infrared spectrometer (FTIR); surface morphology by scanning electron microscope (SEM); optical properties by UV-Visible-IR spectrometer and wettability by the contact angle.

Electronic Materials and Photonics Division

Room 101A - Session EM+2D+AN+MI+MP+NS-TuA

Solar/Energy Harvesting and Quantum Materials and Applications

Moderators: Yohannes Abate, Georgia State University, Nicholas Strandwitz, Lehigh University

2:20pm **EM+2D+AN+MI+MP+NS-TuA1 Plasmonic Metasurface Electrodes for Excitonic Solar Cells.***, **Deirdre O'Carroll**,* Rutgers, the State University of New Jersey **INVITED**

Excitonic organic solar cell technologies, while not currently competitive with inorganic-semiconductor analogues, can exhibit very small device embodied energies (due to comparatively low temperature and low energy-use fabrication processes), which is of interest for minimizing overall device cost and energy-payback time. To improve energy conversion efficiency in thin-film excitonic organic solar cells, light management using nanophotonic structures is necessary. Here, our recent work on improving light trapping in deeply-subwavelength excitonic organic semiconductor films using plasmonic metasurfaces will be presented. Numerous exciton-metasurface interaction phenomena, such as absorption-induced scattering, exciton-plasmon coupling and morphology-dependent surface plasmon light-trapping are observed to give rise to improved light trapping at different regions of the solar spectrum. Additionally, an approach to achieve the theoretical limits to the efficiency of excitonic organic photovoltaics (~22%) will be proposed that involves control of radiative recombination rate, and optimization of both photoluminescence quantum efficiency and photon recycling in organic semiconductor thin-films.

3:00pm **EM+2D+AN+MI+MP+NS-TuA3 Photoemission Electron Microscopy as a New Tool to Study the Electronic Properties of an Inhomogeneous Semiconductor for Photovoltaics***, M. Berg,* Sandia National Laboratories*; J. Kephart, A. Munshi, W.S. Sampath,* Colorado State University*; **Taisuke Ohta**, C. Chan,* Sandia National Laboratories

The energy positions of the valence and conduction electronic states with respect to the vacuum level are essential parameters to evaluate how the band gaps of semiconductors or Fermi-levels of metals line up with respect to each other. Such electronic structures of materials can be determined using photoemission spectroscopy (PES). PES measurements, however, remain challenging for inhomogeneous materials with nano- to micrometer lateral dimensions due to its mesoscopic probing area, typically no less than several microns. Photoemission electron microscopy (PEEM) is a cathode lens electron microscopy technique that combines photoemission imaging with spectroscopic modes of operation to provide PES spectra from areas less than one micron in size. Here, we present PEEM studies of the electronic structure of polycrystalline cadmium telluride (CdTe) thin films, a test case to examine the applicability of this new microscopic approach to photovoltaic materials. Post-deposition $CdCl_2$ treatment of CdTe is known to increase photovoltaic efficiency. However, the precise chemical, structural, and electronic changes that underpin this improvement are still debated. In this study, PEEM was used to spatially map the vacuum level and ionization energy of CdTe films, enabling the identification of electronic structure variations between grains and grain boundaries. *In vacuo* preparation and inert environment transfer of oxide-free CdTe surfaces isolated the separate effects of $CdCl_2$ treatment and ambient oxygen exposure. Qualitatively, grain boundaries displayed lower work function and downward band bending relative to grain interiors, but only after air exposure of $CdCl_2$-treated CdTe. This study highlights the importance of probing the spatially varying electronic structure, elucidating the concurrent impacts of processing steps ($CdCl_2$ treatment and oxygen exposure) to develop a comprehensive picture of local electronic structure in an inhomogeneous semiconductor.

The PEEM work was performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility (DE-AC04-94AL85000). M. B. & C. C. were supported by a U.S. DOE-EERE SunShot BRIDGE award (DE-FOA-0000654 CPS25859). T. O. was supported by the CINT user program and Sandia LDRD. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. The views expressed in the article do not necessarily represent the views of the US DOE or the US Government.

3:20pm **EM+2D+AN+MI+MP+NS-TuA4 Modification of Bandgap for Lead-Free Double Perovskite $Cs_2AgInCl_6$ with Bi Doping***, **Hassan Siddique**, H. Da, X.Q. Wang, R.C. Dai, Z.P. Wang, Z.J. Ding, Z.M. Zhang,* University of Science and Technology of China

Lead halide perovskites have the excellent luminescent properties but exist some vital disadvantages such as instability and Pb toxicity. Lead-free double perovskites draw attention due to a possible candidate for environment-friendly materials. Direct bandgap lead-free halide of $Cs_2AgInCl_6$ is one of them. [1] In this work Bi doping $Cs_2AgInCl_6$ (CAIC) was successfully prepared. Bi dopant above 15% CAIC can restrict the parity forbidden transition responding to sub absorption peak around 600 nm.[2] On the other hand, the intensity of photoluminescence enhances with the increasing Bi dopant and touches the maximum around 30% doping, then gradually loses its intensity with further doping due to the mechanism of the concentration quenching at room temperature. Bi doping in CAIC can also modify the band gap. The absorption spectra indicate that the band gap reduces from 3.10eV without Bi doping to 2.68eV for $Cs_2AgIn_{0.30}$ $Bi_{0.70}Cl_6$. PL decay life time reveals the good intrinsic excitonic feature with less defect trappers [3]. Average life time for $Cs_2AgIn_{0.70}$ $Bi_{0.30}Cl_6$ is 490 ns which is least among all other $Cs_2AgIn_{(1-x)}Bi_xCl_6$ doping. Thermogravimetric analysis (TGA) result reveals thermal stability of $Cs_2AgIn_{0.30}$ $Bi_{0.70}Cl_6$ for the high-temperature 506^{o}C. The Bi doping can decrease the band gap, restrict defect states, enhance PL and improve stability; these good performances make $Cs_2AgIn_{(1-x)}Bi_xCl_6$ more suitable for optoelectronic properties.

4:20pm **EM+2D+AN+MI+MP+NS-TuA7 Optimized (Quantum) Photonics***, **Jelena Vuckovic**,* Stanford University **INVITED**

Photonics has numerous applications ranging from optical interconnects, classical and quantum computing, to sensing (such as LIDAR and AR), and imaging. However, the state of the art photonics is bulky, inefficient, sensitive to environment, lossy, and its performance is severely degraded in real-world environment as opposed to ideal laboratory conditions, which has prevented from using it in many practical applications. Therefore, it is clear that new approaches for implementing photonics are crucial.

We have recently developed a computational approach to inverse-design photonics based on desired performance, with fabrication constraints and structure robustness incorporated in design process [1,2]. Our approach performs physics guided search through the full parameter space until the optimal solution is reached. Resulting device designs are non-intuitive (see Figure), but are fabricable using standard techniques, resistant to temperature variations of hundreds of degrees, typical fabrication errors, and they outperform state of the art counterparts by many orders of magnitude in footprint, efficiency and stability. This is completely different from conventional approach to design photonics, which is almost always performed by brute-force or intuition-guided tuning of a few parameters of known structures, until satisfactory performance is achieved, and which almost always leads to sub-optimal designs.

Apart from integrated photonics, our approach is also applicable to any other optical and quantum optical devices and systems. In recent years, color centers in diamond and silicon carbide (SiC) have emerged as a possible platform for implementation of quantum circuits [3,4]. We demonstrate how such quantum hardware can also be optimized to be robust, efficient, and scalable.

References

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5:00pm **EM+2D+AN+MI+MP+NS-TuA9 Optical Properties of Single Silicon Vacancies in 4H-SiC***, H.B. Banks,* National Research Council Postdoc residing at the Naval Research Laboratory*; O. Soykal,* Sotera Defense Solutions, Inc, residing at the Naval Research Laboratory*; S.P. Pavunny, R.L. Myers-Ward, D.K. Gaskill,* ***Samuel Carter****,* U.S. Naval Research Laboratory

Defects in wide bandgap materials have generated substantial interest as promising systems for quantum information and quantum sensing due to bright, stable optical emission that is often coupled to long-lived spin states. One promising defect system is the silicon monovacancy in SiC (V_{Si}), which has a spin-3/2 ground state that can be optically polarized and maintain long spin coherence times even at room temperature. SiC is an attractive material in terms of mature growth and fabrication technology and also has a low natural abundance of nuclear spins, which reduces spin dephasing. While significant work has been performed to study the spin properties of V_{Si} for ensembles and even single defects, the optical properties and their connection to the spin system are less developed. Here we report on high resolution optical spectroscopy of single V_{Si} defects, specifically V2 defects, at low temperatures. Using laser excitation spectroscopy, the zero phonon line (ZPL) transitions corresponding to the $m_s=\pm1/2$ and $m_s=\pm3/2$ spin states are resolved, with a linewidth down to 70 MHz and a splitting of 1 GHz. While there is significant variation in the transition energies from one defect to another, the splitting of these lines is very uniform. We also find that emission from the V2 defect under resonant excitation of these lines rapidly decays on two very different timescales. Slow decay on a 10 ms timescale is attributed to photoionization of V_{Si} and can be prevented by periodically exciting the defect with a second laser at 745 nm. Fast decay on a µs or shorter time scale occurs due to a combination of intersystem crossing and spin polarization of the ground state. A significant difference in the decay rates of the two transitions is observed, which gives rise to spin-dependent photoluminescence intensity and non-resonant optical spin polarization. These results further our understanding of the connection between the optical and spin properties of this defect system that are necessary to optically control and readout the spin system as well as to develop a spin-photon quantum interface.

5:20pm **EM+2D+AN+MI+MP+NS-TuA10 Photoluminescence Studies on Patterned Silicon Vacancy Defects in Li Ion Implanted 4H-SiC for Scalable Quantum Device Applications***,* ***Shojan Pavunny****,* U. S. Naval Research Laboratory*; S.G. Carter, H.B. Banks, R.L. Myers-Ward, P. Klein,* U.S. Naval Research Laboratory*; E.S. Bielejec,* Sandia National Laboratories*; M.T. DeJarld, A.S. Bracker, E.R. Glaser, D.K. Gaskill,* U.S. Naval Research Laboratory

Recently, silicon vacancy defect centers (V_{Si}) in the CMOS compatible wide bandgap semiconductor SiC hexagonal polytypes have drawn great research interest for future applications in scalable quantum information and quantum sensing mainly due to their high electronic spin (S = 3/2) with a long coherence time at room temperature. Realization of future densely integrated quantum devices will greatly benefit from the ability to deterministically induce the desired V_{Si} density at the optimal location in the three-dimensional solid-state matrix with nanometer accuracy and excellent optical properties. With this motivation, we demonstrate targeted formation of arrays of V_{Si} ensembles as well as single defects in high-quality 4H-SiC epilayers by a direct, maskless focused ion beam implantation technique with a designed lateral separation of ~5 µm and a ~25 nm spot size. We have carried out high-resolution optical spectroscopy studies ($E\perp c$ and $E\parallel c$) on these arrays, in which lithium ions are implanted at doses varying from 10^{12} – 10^{15} Li/cm^2 at a fixed energy of 100 keV to a depth of ~400 nm from the surface. Photoluminescence intensity and defect conversion yield with dose, photostability, fluorescence saturation, and V_1:V_1' intensity evolutions with temperature and excitation power were investigated. Results obtained from temperature dependent photoluminescence studies can provide key insights in the design and fabrication of scalable and reproducible three dimensional SiC quantum hybrid devices including photonic crystal cavities.

5:40pm **EM+2D+AN+MI+MP+NS-TuA11 Processing of Cavities in SiC Material for Quantum Technologies***,* ***Rachael Myers-Ward****, K. Hobart, K.M. Daniels, A.J. Giles, M.J. Tadjer, L.E. Luna, F.J. Kub, S.P. Pavunny, S.G. Carter, H.B. Banks, E.R. Glaser,* U.S. Naval Research Laboratory*; P.B. Klein,* Sotera Defense Solutions*; K. Qiao, Y. Kim, J. Kim,* Massachusetts Institute of Technology*; D.K. Gaskill,* U.S. Naval Research Laboratory

Silicon carbide is a material of interest for quantum computing and sensing applications owing to deep point defect centers with long spin coherence times (which characterizes the lifetime of the qubit), specifically the V_{Si} [1], divacancies [2] and nitrogen-vacancy centers [3]. These spin qubits have been isolated and coherently controlled, where V_{Si} have T_2 coherence times up to 100 µs [4] and divacancies to 1 ms [2], making these two defects of most interest to date. While the current spin coherence times have been shown to be as long as 1 ms, further improvements are needed to fully realize the potential of SiC for quantum applications. In this work, we create V_{Si} in epitaxial SiC and investigate fabricating the layers into microstructures suitable for using the V_{Si} photoluminescence (PL) emission. We have found 4H-SiC epitaxial layers grown under standard growth conditions and with varying doping densities from 10^{14} to 10^{18} cm^{-3} have no measureable V_{Si} present, as determined by confocal PL. To introduce V_{Si}, we used 2 MeV electron irradiation in doses ranging from 0.75 to 75 kGy. This results in V_{Si} PL ranging from single to ensemble emission within the confocal volume. Hence, we are able to tune the vacancy concentration.

In order to improve the indistinguishable photons from the V_{Si} and/or divacancies for real applications, photonic crystal cavities (PCC) are used to tune the emission energy [4]. Our PCC design consists of a planar array of cylindrical holes approximately 220 nm wide in a slab of SiC, ~300-500 nm thin having an area 50 x 50 µm^2, similar to [4]. To maximize the PCC quality factor, the slab should have a large index of refraction difference on the top and bottom; i.e., an air gap is desired under the slab. To achieve this goal, we have identified four fabrication methods to create the PCC. One of these techniques is to use remote epitaxy as an innovative approach which entails growing epitaxial graphene on a SiC substrate by means of Si sublimation. Silicon carbide is then grown on a monolayer of graphene to the desired film thickness [5]. This thin SiC layer is then transferred, facilitated by the weak van der Waal forces at the graphene/SiC substrate interface, to a substrate more amenable to cavity fabrication. All four fabrication methods will be presented in detail.

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6:00pm **EM+2D+AN+MI+MP+NS-TuA12 Investigation of Localized Electronic structures of PbSe Quantum Dot Superlattice on a Highly Oriented Pyrolytic Graphite (HOPG)***,* ***Il Jo Kwak****, S. Ueda,* University of California at San Diego*; A. Abelson, C. Qian, M. Law,* University of California, Irvine*; A.C. Kummel,* University of California at San Diego

Lead-Chalcogenide quantum dots are of interest due to the facility of adjustment of their electrical and optical properties. Using a colloidal self-assembly technique, extended arrays of nanocrystal QDs superlattices can be generated. The quantum confinement within individual QDs in the superlattice is relaxed and delocalization of wave functions occurs due to coupling of the QDs. In the QD solids, bulk-like electronic bands with a bandwidth of 100~200 meV are expected to form which yield much higher carrier mobility and diffusion length compared to weakly-coupled QDs; however, the electronic properties of such highly ordered QD arrays are not fully understood. The local density of state of a highly ordered monolayer PdSe superlattice was investigated by low temperature scanning tunneling microscopy.

A monolayer of PbSe QDs was prepared using the Langmuir Schaefer deposition technique. First, oleate-capped PbSe QDs dispersed in hexane were drop casted onto diethylene glycol surface. After the hexane was evaporated, a (111) in-plane oriented polycrystalline FCC superlattice was formed on the diethylene glycol surface. NH_4SCN solution was applied onto the oleate-capped PbSe superlattice film. The injection of NH_4SCN initiates the ligand exchange and phase transformation from an FCC to a simple cubic structure superlattice. A monolayer QD superlattice was prepared on a HOPG substrate. Afterward, the HOPG sample was loaded into a commercial UHV scanning tunneling microscopy chamber with a base pressure of $1x10^{-10}$torr. The sample was annealed to remove hydrocarbons and ligands from the surface. The topography of the QDs was observed with a tungsten tip. The STM images were acquired in constant current mode.

STM imaging showed the PbSe QD monolayer had 4-fold symmetry with an average inter QD spacing of 7nm. It is also found the height fluctuation of the QDs was 1nm indicating size variation of the QDs and imperfect crystal structure of the superlattice. Scanning tunneling spectroscopy was performed to investigate the electronic structure of the PdSe QDs using a variable z-mode with an external lock-in amplifier in the bias range of -2 to 2V. Single site STS showed resonant peaks from molecular orbitals of QDs before the ligand exchange process; however, the peaks were not observed after the ligand exchange due to necking between the QDs in the superlattice. In addition, the size of band gap was decreased as increasing the number of nearest neighboring QDs due to necking between QDs. Layer 2 QDs showed more p-type behavior than layer 1 QDs possibly due to the band bending effect at the interface of HOPG and QD superlattice.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 201A - Session HC+SS-TuA
A Tale of Two Scales: Catalytic Processes and Surface Science

Moderator: Ashleigh Baber, James Madison University

2:20pm **HC+SS-TuA1 CO_2 Reduction on the Surface of Cu/TiO_2 NPs Supported on Graphite Studied using Ambient Pressure-XPS and Differential Electrochemical Mass Spectrometer***, **Djawhar Ferrah**, A. Haines, R.P. Galhenage,* University of California at Irvine*; A. Javier,* California Institute of Technology*; J.P. Bruce,* University of California at Irvine*; M. Soriaga,* California Institute of Technology*; J.C. Hemminger,* University of California at Irvine

Metal supported on metal oxide (M1/MO) catalyst systems are widely used in industry for the hydrogen production and CO_2/CO conversion to useful fuels. If incontrovertible evidence were founded for the role of the interface in the improvement of catalytic CO_2 hydrogenation efficiency, it would still be an incomplete understanding on the nature of the active sites and associated reaction pathways, namely reactive species adsorption, dissociation and/or activation and intermediate formation stability. The modulation of the reaction selectivity, through the synthesis of catalysts that exhibit specific active sites, is required to design «smart » catalytic systems. Therefore, the investigation of catalytic reactions under real conditions, to illustrate the relation between properties at the atomic level of the surface and reactivity, is needed. In this context, a model catalyst based on Cu/TiO_2 nanoparticles (NPs) supported on graphite (HOPG), have been synthesized and fully characterized using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS). Using physical vapor deposition (PVD), a high density of 15 nm TiO_2 NPs are deposited on HOPG and are used to support Cu NPs. TEM studies reveal that most of the TiO_2 NPs have a rutile structure and display mainly (110) vicinal surface, which is favorable for CO_2 adsorption. A formation of thin layer of graphitic carbon at surface of TiO_2 NPs is also reported. Photodeposition of Cu on TiO_2 NPs by irradiating the band gap of TiO_2 in a $CuCl_2$ solution has been studied. In the present work, two different catalytic aspects for CO_2 reduction on CuO_x/TiO_2 NPs on HOPG systems will be reported: (1) thermocatalytic CO_2 hydrogenation and (2) electrochemical CO_2 hydrogenation. Efforts have been devoted to exploring different surface chemistry effects, as well as the oxidation states of Cu NPs (Cu_2O, Cu, and Cu_2O@Cu) with diameters ranging from 2 to 5 nm and TiO_2 surface encapsulation with thin layer of graphited carbon, on the CO_2 reduction mechanism in the temperature range of 300-550 K using Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) at the National Synchrotron Light Source II (NSLS-II). Similarly, the CO_2 reduction on CuO_x/TiO_2 NPs on HOPG electrodes in aqueous $KHCO_3$ has been investigated using a Differential Electrochemical Mass Spectrometer (DEMS) to evaluate the reaction products. Ongoing Infrared reflection-absorption spectroscopy (IRRAS), and AP-XPS experiments on electrochemical CO_2 reduction will be introduced.

2:40pm **HC+SS-TuA2 Influence of Bi and Sb on the Structure of Pd-based Catalysts***, **Joo Kang**, W.-S. Lee, P.R. Vlasak,* The Dow Chemical Company*; A.V. Kirilin,* The Dow Chemical Company, Netherlands*; H. Clements, C. Menzies, S. Yusuf,* The Dow Chemical Company

Oxidative transformation of aldehydes to corresponding esters is a reaction of significant importance. Catalytic oxidative esterification of aldehydes and alcohols in the presence of heterogeneous catalysts is an attractive method for production of esters. Reaction can be carried out in the presence of palladium or platinum often with co-components to improve performance.

The influence of 4d and 5d metal promoters on Pd based catalysts was investigated using a suite of structure probing techniques including x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectroscopy (ToF-SIMS), and X-ray Absorption Spectroscopy (XAS). Results on supported Pd, Pd-Bi and Pd-Sb catalysts allow new insight into active Pd structure and role of the promoters on Pd structure. We present formation of bimetallic phase in both Bi and Sb promoted Pd catalysts and discuss implication on catalytic performance.

3:00pm **HC+SS-TuA3 The Molecular Surface Chemistry Approach to Heterogeneous Catalysts***, **Peter Stair**,* Northwestern University **INVITED**

The traditional route to solid catalyst materials involves solution phase deposition or liquid-surface reactions. Examples include impregnation, deposition-precipitation, and solution phase grafting of molecular precursors. Atomic Layer Deposition (ALD) is a gas-solid deposition methodology having enormous potential for the synthesis of advanced heterogeneous catalysts with control of composition and structure at the atomic scale. The ability of ALD to produce conformal oxide coatings on porous, high-surface area materials can provide completely new types of catalyst supports. At the same time ALD can achieve highly uniform catalytically active metal and oxide phases with (sub-) nanometer dimensions. This lecture will provide examples from the laboratories at Northwestern University and Argonne National Laboratory of ALD used to synthesize oxide supports, catalytic oxide overlayers, single-site catalysts, metal nanoparticles, and new porous structures.

4:20pm **HC+SS-TuA7 Formation and Stability of Subsurface Oxygen on Ag(111)***, **Marie Turano**,* Loyola University Chicago*; S. Isbill, S. Roy,* University of Tennessee Knoxville*; R.G. Farber,* Loyola University Chicago*; E.V. Iski,* University of Tulsa*; D.R. Killelea,* Loyola University Chicago

A long-standing challenge in the study of heterogeneously catalyzed oxidation reactions on silver surfaces is the determination of what surface species are of greatest chemical importance. This is due to the coexistence of several different types of oxygen on oxidized silver surfaces. A further wrinkle is subsurface oxygen (Osub). Osub are O atoms dissolved into the near surface of a metal, and are expected to alter the surface chemistry and structure, however, these effects have yet to be well characterized. To better understand the interactions of oxidized silver surfaces, synergy between experimental and theoretical studies is necessary. We have studied oxidized Ag(111) surfaces after exposure to gas-phase O atoms using a combination of surface science techniques to determine the resultant surface structure. We observed that once 0.1 ML of Osub has formed, the surface dramatically, and uniformly, reconstructs to a striped structure at the expense of all other surface structures. Furthermore, Osub formation is hindered at temperatures above 500 K. We also observed a coexistence of several surface oxides at intermediate deposition temperatures (475-525K), and the predominance of the p(4x5√3) surface reconstruction at elevated temperatures. Recent DFT-calculated desorption energies of O atoms from Ag(111) agree well with experimentally-derived desorption energies, and provide qualitative insight into the formation and stability of Osub at different oxygen coverages.

4:40pm **HC+SS-TuA8 Mechanistic Insights into Catalytic Transfer Hydrogenation and Decarbonylation of Aromatic Aldehydes on P_x-Ru(0001)***, **Abinaya Sampath**, D.W. Flaherty,* University of Illinois at Urbana-Champaign

Aromatic aldehydes constitute a significant weight fraction of bio-oil.Transition metal catalysts can hydrogenate these aldehydes using either gaseous H_2 or organic donors to produce valuable chemicals that may replace conventional petroleum derivatives. Here, we study selective decarbonylation of aromatic aldehydes (furfural and benzaldehyde) over Ru(0001) and P_x-Ru(0001) to determine how phosphorus introduces new reaction pathways, such as catalytic transfer hydrogenation (CTH) steps between organic reactants. The catalytic properties of Ru(0001) and P_x-Ru(0001) were probed with temperature programmed reaction (TPR) of furfural, benzaldehyde, and isotopically labeled forms of furfural under ultra-high vacuum conditions with Ru(0001) single crystal. P_x-Ru(0001) is formed by exposing Ru(0001) to 2.5 L of PH_3 at 300 K followed by flash annealing to 1400 K. The treatment produces a surface with an atomic ratio of P: Ru of ~0.4, determined by Auger electron spectroscopy.

On $P_{0.4}$-Ru(0001), ~68% of furfural adsorbed at 100 K decarbonylates to furan and CO, whereas on Ru(0001), furfural decomposes completely to CO, H_2, and C-atoms. Similarly, benzaldehyde decarbonylates to benzene with a selectivity that is 12-fold greater over $P_{0.4}$-Ru(0001) than on Ru(0001). Together, these results suggest that, P-modification of Ru(0001) results in selective decarbonylation of aromatic aldehydes. Charge transfer from Ru to P results in reduced electron back donation from Ru to the adsorbates, and causes adsorbates to interact more weakly with $P_{0.4}$-Ru(0001) than with Ru(0001). These electronic modifications reduce the extent of dissociative reactions leading to selective decarbonylation of aromatic aldehydes, although ensemble effects may also contribute.

TPR of furfural on $P_{0.4}$-Ru(0001), pre-covered with D* atoms, yields five times more per-hydrogenated furan (C_4H_4O) than mono-deuterated furan (C_4H_3DO), which demonstrates that the CTH does not involve chemisorbed H*-atoms. On $P_{0.4}$-Ru(0001), TPR of isotopically labeled furfural (C_4H_3O-CDO) forms two furan isotopologues (C_4H_4O, and C_4H_3DO). In addition, C_4H_3DO formed desorbs at a temperature 20 K higher than C_4H_4O, which indicates that intermolecular H-transfer determines the rate of furan formation. The comparisons of labeled furan products show that these critical H-atoms originate from the furfural ring and the carbonyl group of furfural. Hence, $P_{0.4}$-Ru(0001) is more selective for decarbonylation of aromatic aldehydes over Ru(0001), and the addition of phosphorus atoms facilitates CTH steps that do not occur on metallic Ru(0001).

5:00pm **HC+SS-TuA9 Hot Electron Flux under Methanol Oxidation on Pt/TiO_2 Catalytic Nanodiode; Intrinsic Relation between Selectivity and Chemicurrent***, Si Woo Lee, S. Lee,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea*; H. Lee,* Institute for Basic Science (IBS), Republic of Korea*; W. Park, Y. Jung, J.Y. Park,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Nonadiabatic electronic excitation in exothermic chemical reactions leads to the flow of energetic electrons with an energy of 1-3 eV which is called “hot electrons”. Direct detection of hot electron flow and observation of its role in catalytic reactions are important for understanding metal-oxide heterogeneous catalysis [1, 2]. Using Pt/n-type TiO_2 Schottky nanodiode, we show the production of hot electron flow generated by methanol oxidation ($P_{methanol}$ 4 Torr and P_{oxygen} at 760 Torr) on Pt thin film, and detect as steady-state hot electron current (chemicurrent) which is generated by exothermic chemical reactions on Pt catalyst surface. Under methanol oxidation, methanol can be converted to CO_2 by full oxidation or methyl formate by partial oxidation of methanol. We show that the activation energy of chemicurrent is quite close to that of turnover frequency, indicating that the chemicurrent was originated from the catalytic reaction on Pt thin film. In addition, the dependence of the partial pressure on the chemicurrent was investigated by varying partial pressure of methanol (1-4 Torr). The result shows that the selectivity toward methyl formate formation is well correlated with the chemicurrent. For fundamental understanding of correlation between selectivity and chemicurrent, we carried out the DFT calculation on the thermodynamic energy for each step, and found that the energy gain for partial oxidation reaction was higher than that of the full oxidation reaction, which is responsible for the higher flux of hot electron under methyl formate formation. We discuss the role of metal-oxide interfaces in determining the catalytic selectivity and chemicurrent yield.

Reference

1. Park, J. Y.; Baker, L. R.; Somorjai, G. A., Role of Hot Electrons and Metal–Oxide Interfaces in Surface Chemistry and Catalytic Reactions. *Chem. Rev.* **2015,** *115* (8), 2781-2817.

2. Park, J. Y.; Kim, S. M.; Lee, H.; Nedrygailov, I. I., Hot-Electron-Mediated Surface Chemistry: Toward Electronic Control of Catalytic Activity. *Acc. Chem. Res.* **2015,** *48* (8), 2475-2483.

5:40pm **HC+SS-TuA11 Non-Innocent Solvents, Hydrogen Transfer, Oxygen Dissociation on Nanoparticles during the Direct Synthesis of H_2O_2***, David W. Flaherty,* University of Illinois, Urbana-Champaign **INVITED**

Direct synthesis of H_2O_2 ($H_2 + O_2 \rightarrow H_2O_2$) could enable on-site, and even *in situ*, H_2O_2 production, which motivates searches for highly selective catalysts and process conditions. H_2O_2 formation rates and selectivities depend sensitively on the addition of other transition metals, adsorption of halides, and solvent identity. The reasons for these changes are not completely understood and are difficult to explain mechanistically.

Rate measurements, X-ray absorption spectroscopy, and computation were conducted for Pd and Pd-based bimetallic clusters to determine the mechanism of this reaction and to understand the reasons why alloying Pd often increases H_2O_2 selectivities. In aqueous alcohols, the change in H_2O_2 and H_2O formation rates with H_2 and O_2 pressures are not consistent with a Langmuirian mechanism, but instead suggest O_2* species react in steps mediated by the solvent. In addition, H_2O_2 formation rates in protic solvents are 10^3 larger than those measured in aprotic liquids and large kinetic isotope effects ($k_H/k_D > 7$) strongly suggest that alcohols serve as reactants in the kinetically relevant steps for $H\text{-}_2O_2$ formation. In parallel, O-O bonds within chemisorbed intermediates cleave to form H_2O with rates that are less sensitive to the solvent identity. Persistent organic surface residues introduce low barrier reaction pathways to reduce O_2* and increase those for O-O dissociation relative to reaction pathways in pure water. These results show that long-standing observations that H_2O_2 forms in greater yields within alcoholic solvent are not explained by simple differences in the solubility of H_2 in the liquid-phase.

Similar rate laws and solvent requirements indicate that these reactions proceed by the same pathways in the presence of strongly binding halide adsorbates and acids. These modifications change barriers for the formation of H_2O (significantly) with lesser effects on barriers for steps that lead to H_2O_2, and are consistent with electronic modifications of Pd active sites by intra-atomic orbital rehybridization or by charge transfer from Pd atoms, respectively. Overall, this work presents evidence for the mechanism for H_2O_2 formation and explains the roles of solvent identity and surface modification strategies on H_2O_2 selectivities.

Manufacturing Science and Technology Group
Room 202B - Session MS+MN-TuA

IoT Session: Challenges of Sensor Manufacturing for the IoT

Moderator: Robert Lad, University of Maine

2:20pm **MS+MN-TuA1 Manufacturing Strategies for Flexible Hybrid Electronics***, Scott Miller,* NextFlex **INVITED**

Flexible Hybrid Electronics (FHE) combines technologies and manufacturing capabilities from the worlds of printing and additive manufacturing; flexible, bendable, stretchable, and 3D substrates; and conventional silicon integrated circuits to bring novel form and function to high-performing electronic devices. The US manufacturing ecosystem for FHE is rapidly growing and applications of FHE devices are being advanced in areas as diverse, and yet overlapping, as human health and performance monitoring, antennas and wireless communications, soft robotics, structural health management, and IoT. A single device build can require solving substrate challenges, printing functional conductors, resistors, and dielectrics, placing discrete passives, attaching bare-die integrated circuits using conductive adhesives, integrating a power supply, and encapsulating the entire device. As a Manufacturing Institute, NextFlex works with its members on technologies that have passed the applied research stage to advance their readiness for manufacturing and position them for product development. This talk will explore challenges and opportunities in FHE, including translating designs to manufacturing, material and device characterization, availability of material and process data, and scaling processes to high-rate manufacturing. Approaches to address these challenges will be discussed and example projects related to IoT will be presented.

3:00pm **MS+MN-TuA3 Enabling Smart and Connected Living through High Volume Roll to Roll Manufacturing***, Enid Kivuti,* Sheldahl Flexible Technologies **INVITED**

Enabling Smart and Connected Living through High Volume Roll to Roll Manufacturing

The presentation will provide an overview of automated, continuous processing technologies available in the manufacture of Flexible Printed Electronics for the Internet of Things applications. Beginning with material choice, and concluding with proposed useable devices, we will explore Additive, Subtractive and Hybrid technologies and the governing design rules. We will review recent industry developments that enable finished products to improve user experience. Finally, we will provide examples of scalable IOT applications that meld the use of existing capital assets with the rapidly evolving industry options to deliver improved performance at a lower total cost of ownership.

Key Words:

Thin Film Vacuum Deposition

Printed Electronics

Hybrid Technology

Sensors

Medical

Automotive

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4:20pm **MS+MN-TuA7 New Generation Chemical and Biological Sensors: From New Ideas to Manufacturable Products in the era of Internet of Things and Industrial Internet*, Radislav Potyrailo,*** General Electric Global Research Center **INVITED**

Modern monitoring requirements of gases and liquids for demanding applications such as medical diagnostics, environmental surveillance, biopharmaceutical process control, industrial safety, and homeland security push the limits of existing detection concepts where we may reach their fundamental performance limits. Thus, without violating the laws of physics, chemistry, and electronics, we need to develop new practical detection concepts and instruments. We are developing new generation of handheld, wireless, and wearable sensors that bridge the gap between the existing and required sensing capabilities. This talk will stimulate your scientific and engineering senses by posing several fundamental and practical questions on principles of chem/bio sensing and by demonstrating on how we address these questions in the developments of sensors with previously unavailable capabilities with examples of strategies of bringing new ideas from their initial lab tests, to field validation, and to final products.

5:00pm **MS+MN-TuA9 The Unique Challenges Implantable Sensor Manufacture*, Kimberly Chaffin,*** *S. Terry,* Medtronic plc **INVITED**

Sensors onboard today's implantable medical devices monitor the critically ill and trigger the delivery of life sustaining and saving therapies. As medicine moves from retrospective treatment to predict and prevent, a transition enabled, in part, by the Internet of Things (IoT), sensors will no longer only be operational in the critically ill, but in all of us. In the future, sensors will have the sole purpose of measuring physiological signs and providing patient centric feedback to prevent future events. Setting aside the psychological challenges of receiving a long-term implant for prevention, this transition to prevent and predict is making the medical device industry rethink sensor manufacture, where the device-biological interface is one of several critical factors. The current design paradigm of isolating implantable device circuitry from the biological environment in hermetic titanium cans, largely limiting the signal to electrical feedthroughs, must shift to allow for new sensor modalities. Chemical sensors must detect biomarkers unhindered by the immune response that accompanies every implant. Optical sensors must 'see' into the body. Pressure sensors must employ sensitive diaphragms where the internal device pressure must remain constant and the fibrotic capsule formation associated with the immune response must not dampen sensitivity. In this talk, we will review the critical manufacturing technologies being developed for implantable sensors that predict and prevent.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+AM+MI+MN+SS+TR-TuA

SPM – Probing and Manipulating Nanoscale Structures

Moderators: Renu Sharma, NIST Center for Nanoscale Science and Technology, Carl Ventrice, Jr., SUNY Polytechnic Institute

2:20pm **NS+AM+MI+MN+SS+TR-TuA1 Building Artificial Quantum Matter with Dopant Atoms*, Sven Rogge,*** University of New South Wales, Australia **INVITED**

Atomic-scale engineering reached the level of control where single-atom devices can be reproducibly fabricated with high yield. This talk focuses on the progress of single dopant atom placement in the context of engineered quantum matter. Silicon offers a particularly interesting platform for single dopants because when isotopically purified it acts as a "semiconductor vacuum" for spins. This leads to extraordinary coherence that is used to realise donor atom based qubits. Spatially resolved tunnelling experiments reveal the spectrum and quantum state image of single atoms and tunnel coupled arrangements of atoms. These measurements grant access to the wavefunction of donors in the silicon lattice that makes it possible to pinpoint the dopants to their exact position in the lattice that is essential in the evaluation of engineered quantum matter. A first step towards engineered Hamiltonians for Fermionic systems in the form of atomic chains was taken where interacting dopants were employed to simulate a two-site Hubbard Hamiltonian at low effective temperatures with single-site resolution. Quasi-particle tunnelling maps of spin-resolved states with atomic resolution reveal interference processes from which the entanglement entropy and Hubbard interactions are quantified. We will present dopant based multi-electrode devices fabricated by the scanning probe hydrogen depassivation and decoration technique where the quantum state of the device can be manipulated and imaged in situ. The aim of this work is to build a two dimensional array of up to 30 spins in the solid state to implement complex highly correlated systems.

3:00pm **NS+AM+MI+MN+SS+TR-TuA3 Scanning Tunneling Microscopy Study of Structure Control of a Nanocarbon Catalyst through a Surface-Activated coupling Reaction*, Jeremy Schultz,*** *P. Whiteman, N. Jiang,* University of Illinois at Chicago

In order to optimize nanocarbon materials for metal-free catalysis, the structure must be controlled and characterized at the nanoscale. One method for the bottom-up assembly of nanocarbon catalysts is through an Ullmann-type coupling reaction induced by a metal substrate, where a halide leaving group allows covalent intermolecular coupling. Scanning tunneling microscopy has been applied to a fundamental study of 3,6-dibromo-phenanthrequinone (DBPQ), a molecule selected for its catalytically active diketonic groups. Conjugated polymers formed from DBPQ have been found to be capable of catalyzing alkane oxidative dehydrogenation (ODH) reactions as well as nitrobenzene (NB) reduction reactions.

Different surfaces were investigated for their role in the surface-activated coupling reaction. Intact monomer molecules were found to self-assemble through hydrogen and halide interactions on Ag(100), resulting in well-packed molecular islands which impacted the organometallic structure ultimately formed after reaction. On Au(100), two competing intermediate dimers were observed resulting from a chiral covalent bond between base DBPQ molecules. Cis dimers were found to result in reaction products that became stuck as tetramers without the potential for further polymerization. Utilization of increasing coverage and a new surface identity that arose from the leaving Bromide resulted in selective formation of longer conjugated polymer chains composed of trans dimers. This study characterizes the ability of initial self-assembly and leaving groups to steer reaction dynamics and control the structure of a nanocarbon catalyst.

3:20pm **NS+AM+MI+MN+SS+TR-TuA4 Detecting the Tip Shape Dependence of the Plasmonic Photon Emission under STM*, Songbin Cui,*** Pohang University of Science and Technology, Republic of Korea*; U. Ham,* Institute for Basic Science (IBS), Republic of Korea*; T.-H. Kim,* Pohang University of Science and Technology, Republic of Korea

Photon signal can be enhanced significantly by modifying the plasmonic nanocavity. This enhancement becomes an important issue in super-resolution microscopy and high resolution spectroscopy, such as scanning tunneling microscopy (STM) electroluminescence [1], surface enhanced Raman spectroscopy, tip enhanced Raman spectroscopy [2], and so on. Low temperature STMs can allow us to achieve less than 1nm tip-sample gap stably. This gap-mode plasmonic nanocavity between an STM tip and surface realizes sub-molecular photon spectroscopy [1]. A few works demonstrated that light emission signal can be effectively enhanced by certain resonant plasmonic spectral peaks, which can be modified by tip indentation [2] and showed theoretically that the larger tip aperture causes a blue shift and the shaper apex curvature results in higher intensity in a photon spectrum [3]. However, the tip shape dependence of the plasmonic nanocavity remains unclear. In this work, we experimentally present the role of tip shape in surface plasmonic light emission. We have used Ag tips and a Ag(100) substrate, and photon signals have been measured from both side of the STM tip simultaneously. We dipped STM tips into the substrate with controlling the dipping depth and the lifting speed in order to change the tip shape, and then, the tip shape subsequently was checked through STM profiles. We found that changing small parts of tip apex (<3nm tip direction) can differ the photon spectrum significantly. Furthermore, the plasmonic photon emission from different direction from a STM tip could be quite different due to tip shape asymmetry. This finding can help us to tune the plasmonic photon emission spectra more efficiently.

[1] R. Zhang et al., Nature 498, 82–86 (2013).

[2] Z. C. Dong et al., Nature Photonics 4, 50–54 (2010).

[3] J. Aizpurua et al., Physical Review B 62, 2065-2073 (2000).

4:20pm **NS+AM+MI+MN+SS+TR-TuA7 Advances in SPM Methods for Energy-relevant Materials***, **Marina Leite,*** University of Maryland College Park **INVITED**

The scientific understanding of nanoscale materials and devices is continuously growing ever since atomic force microscopy (AFM) has enabled us to image these systems at similar length scale. Specifically, there is a pressing need for functional imaging as energy-relevant technologies are becoming dominated by nano- and mesoscale constructs. In this presentation I will review my group's recent research discoveries based on new AFM methods to measure and determine how the electrical, chemical, and/or optical properties influence overall photovoltaic device behavior [1,2]. We realize novel functional imaging AFM-based methods to elucidate the driving forces for the dynamic response of the perovskites upon and post-illumination [3], and polycrystalline materials for solar cells [4,5]. We map nanoscale variations in open-circuit voltage Voc > 300 mV under 1-sun illumination, not revealed by conventional AFM tools. Using fast-KPFM (16 seconds/scan) while maintaining high spatial sensitivity, we map, in real-time, the dynamics of the Voc in perovskite solar cells with spatial resolution < 100 nm. Unexpectedly, we identify a 'residual Voc' post-illumination, attributed here to iodine ion migration, a process that takes place in a time scale of several minutes. We foresee our functional imaging tool to be implemented in the identification of stable perovskite compounds, ranging from lead-free and non-toxic alternatives to new options for tandem designs.

[1] *ACS Energy Letters* **2**, 2761 (2017). Invited Review.

[2]*ACS Energy Letters* **2**, 1825 (2017). Invited Perspective

[3] *Nano Letters***17**, 2554 (2017).

[4] *ACS Energy Letters***1**, 899 (2016).

[5] *Advanced Energy Materials* **5**, 1501142 (2015).

5:00pm **NS+AM+MI+MN+SS+TR-TuA9 Coherent Electrical Contact to Semiconducting Graphene Nanoribbon***, **Chuanxu Ma**, L. Liang,* Oak Ridge National Laboratory*; Z. Xiao,* North Carolina State University*; A.A. Puretzky, K. Hong,* Oak Ridge National Laboratory*; W. Lu, J. Bernholc,* North Carolina State University*; A.-P. Li,* Oak Ridge National Laboratory

High quality electrical contact to low-dimensional semiconductor channel materials is the key to unlocking their unique electronic and optoelectronic properties for fundamental research and device applications. Inappropriate contacts create interfacial states that can pin the Fermi level and form a large Schottky barrier. For 2D transition metal dichalcogenides (TMDs), a route to a high-performance contact has recently been proposed by using a phase transition that converts a hexagonally packed semiconductor (2H) phase into a distorted octahedrally packed metallic (1T') phase. However, a similar approach is not available for 1D materials. Conceptually, an ideal contact would be a metal-semiconductor interface formed with native covalent bonds without introduction of any structural or electronic boundaries. Realization of such a seamless contact in 1D materials such as graphene nanoribbons (GNRs) requires atomically precise development of a heterostructure from well-defined atomic or molecular precursors.

Here we report on a successful approach for making seamless contacts in 1D materials through the formation of GNR staircase heterostructure. The coherent staircase is made of GNRs with widths varying from 7, 14, 21 and up to 56 carbon atoms. The graphitic heterostructures are synthesized by a surface-assisted self-assembly process with a single molecular precursor. While the 7-atom-wide GNR is a large-gap semiconductor, the conjugated wide GNRs are either quasi-metallic or small-gap semiconductors, similarly to the 2D metals. Our study, which combines STM and Raman measurements with DFT calculations, reveals that the heterointerface consists of native sp^2 carbon bonds without localized interfacial states. Such a seamless heterostructure offers an optimal electrical contact to the wide-gap 1D semiconductor.

5:20pm **NS+AM+MI+MN+SS+TR-TuA10 Visualizing Coordination Structures of Small Gas Molecules to Metallo-porphyrin on Au(111) Using Scanning Tunneling Microscopy***, **MinHui Chang,*** Korea University, Republic of Korea*; Y.H. Chang, N.Y. Kim,* Korea Advanced Institute of Science and Technology (KAIST)*; U.S. Jeon, H. Kim,* Korea University, Republic of Korea*; Y.-H. Kim,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea*; S.-J. Kahng,* Korea University, Republic of Korea

Binding reaction between small molecules and metallo-porphyrins play crucial roles in functional processes of biological systems such as oxygen delivery, muscle contraction, and synaptic transmission. Their geometrical structures such as tilted binding of NO to metallo-porphyrin have been recently confirmed by high-resolution scanning tunneling microscopy (STM) images at the single molecule level. Here, we present STM images of further systems, di, tri, and quadra-atomic small molecules, coordinated to metallo-porphyrin on Au(111). We observed square ring, rectangular ring, and center-bright structures for three different small molecules. With the help of density functional theory (DFT) calculations, we reproduce the experimental STM images in the simulated images. Thus, our study shows that geometric structures of small molecules coordinated to metallo-porphyrins can be probed with STM combined with DFT methods.

5:40pm **NS+AM+MI+MN+SS+TR-TuA11 Effects of Dimensionality on the Reactivity of Carboxylic-Acid-Terminated Monolayers***, **Dominic Goronzy**[1], E. Avery, N.M. Gallup,* University of California, Los Angeles*; J. Staněk, J. Macháček, T. Baše,* Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic*; K.N. Houk,* Chemistry and Biochemistry, University of California, Los Angeles*; P.S. Weiss,* University of California at Los Angeles

Self-assembled monolayers (SAMs) are an advantageous construct to modify surfaces and thereby to tune material properties. Three major determinants affect the spontaneous assembly of monolayers: the substrate-monolayer interface, the interactions between the adsorbate molecules, and the monolayer-environment interface. By controlling the exposed functional groups in the SAM, this interface between the surface and the environment can be probed and manipulated. To examine how exposed carboxyl functional groups modulate the properties of SAMs, we have tethered thiol-functionalized carborane cage molecules with and without a carboxyl group to Au{111} surfaces. Using scanning tunneling microscopy (STM), visualization of the *para*-functionalized carboxylic acid carboranethiol was only possible in the form of a mixed monolayer of functionalized and unfunctionalized molecules. These experiments demonstrated that the functionalized molecule adopted the same nearest-neighbor spacings on the surface as the unfunctionalized *para*-carboranethiol, approximately 7.2 Å. By comparison, in our study of carboranethiols with a carboxylic acid functional group attached in the *meta* position, we have been able to image pure functionalized monolayers *via* STM with these molecules showing nearest-neighbor spacings of 8.4 Å, approximately 1 Å larger than the unfunctionalized carboranethiols. Studies of two different isomers of *meta*-carboranethiolate carboxylic acids yielded similar results. In order to examine the effects of changing dimensionality from a 3D solvent system to a 2D thin film, we applied contact angle titration to probe the reactivity of the carboxylic acid head group. These experiments demonstrated a substantial shift from a pK_a of 3-3.2 in solution (3D) to an apparent surface pK_a of approximately 6.5-7.5. Density functional theory calculations were performed to test the effects of desolvation by 2D confinement and showed shifts in pK_a consistent with the experimental data. Together, these results support the concept that the confinement in a 2D environment induces significant changes in reactivity in the molecules, as evidenced by the pK_a shift. Thus, precise positioning of functional groups in SAMs is an important tool to investigate the behavior of surface-confined molecules. This system may also serve as a model to explore dimensionality effects in biological systems, including proteins confined within membranes.

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[1] **NSTD Student Award Finalist**

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room 202A - Session PC+AS+BI+EM+NS+PB+SS-TuA

Progress in Industrial Processes and Characterization of Interfaces and Gas-Solid Interfacial Processes and Characterization

Moderators: Jeffrey Fenton, Medtronic, Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm **PC+AS+BI+EM+NS+PB+SS-TuA1 Near Ambient Pressure XPS as a Standard Tool for True Non-destructive High-throughput Surface Chemical Analysis in Industrial Applications***, **Andreas Thissen**, P. Dietrich,* SPECS Surface Nano Analysis GmbH, Germany*; M. Kjaervik, W.E.S. Unger,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany **INVITED**

Since many decades X-ray excited Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) is a well-accepted standard method for non-destructive chemical analysis of solid surfaces. Over the last years it has been possible to develop XPS instrumentation, that can work far beyond the standard conditions of high or ultrahigh vacuum: Near Ambient Pressure (NAP)-XPS, or ESCA under environmental conditions has become a method, that enters the field of standard surface chemical analysis and thus also the industrial sector. The main reason for this is the extremely fast solid surface analysis of any (degassing or non-degassing) material. Furthermore the environmental conditions around the sample avoid strong surface degradation due to vacuum or photon stimulated desorption. Even during the analysis the sample stays under its equilibrium conditions. Last, but not least the surrounding gas pressures of a couple of mbar acts as built-in charge neutralization on any type of material. This Environmental Charge Compensation (ECC) also decreases the negative influences of the characterization on the sample constitution. All this considered, NAP-XPS is capable of true non-destructive high throughput analysis of sample surfaces. The influence of the ambient conditions on quantification in XPS will be demonstrated and discussed.

After a short summary of the relevant development steps in NAP-XPS instrumentation over the last forty years, this presentation summarizes results of surface chemical analysis on insulating polymer samples, showing the spectroscopic resolution for C1s, F1s and O1s emission lines as a comparison for PET and PTFE. Using this, the application of ECC to bulk insulators (polymeric materials, ceramics), food samples, pharmaceuticals, and different biological materials is demonstrated. The unique ability to measure liquids, like water or aqueous solutions allow for studies of drying processes of liquid containing materials, like paper or absorber materials and finally also opens the field to medical applications, especially to studies of drug uptake into gram-negative bacteria embedded in biofilms.

The last part summarizes methods to analyze materials and device under working conditions. As examples reduction and reoxidation of catalytically active compounds and operando electrochemistry will be presented. An outlook to future industrial applications will be given.

ACKNOWLEDGEMENTS: This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union’s Horizon 2020 research and innovation programme.

3:00pm **PC+AS+BI+EM+NS+PB+SS-TuA3 Surface Modifications in the Medical Device Field – Understanding of Methods to Control Adhesion and Reactions That Materials Undergo***, **Jeffrey Fenton**, B. Theilacker, A. Belu, B. Tischendorf,* Medtronic **INVITED**

Advances in materials chemistry have increased the need for deep understanding of process-material interactions and their role in device or component longevity. In the medical device industry advances are due in part to operating in a federally regulated environment where it may be necessary to understand not only what is the surface chemistry, but how various chemistries interact with the body, what is clean, or where does a foreign material originate. This presentation will highlight case studies where microscopy and surface characterization techniques were successfully applied to help further understand materials performance and interactions with the body.

Polymers used in the medical industry often undergo numerous clinical trials, laboratory testing, and development to understand the body and polymer interactions. The interactions these materials often undergo may potentially be at odds with the bulk material properties. For example, it may be desirable to modify surface properties of PTFE for polymer adhesion or modify a surface chemistry to improve bio compatibility. Methods of polymer surface modification will be presented that either enable or hinder the adhesion of a material to the surface.

Lithium ions generated during battery discharge may undergo interactions with components in or near the battery forming chemistries that may degrade battery performance or material stability. For example, lithium ions are known to interact with silica containing glass to form lithium silicide. The formation of these silicides can degrade the hermetic seal of feedthroughs. One method of studying these interactions is in-situ interfacial reactions characterization. This facile method of generating ions in-situ can be leveraged to understand what reactions may occur at a substrate surface.

The application of surface characterization techniques such as X-ray photoelectron spectroscopy (XPS), Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS), and Scanning Electron Microscopy (SEM) provide unique insights into surface modifications and can help ensure the reliability of medical devices. These techniques support the development and manufacturing of Medtronic products such as packing and perfusion devices to improve processing conditions, understand failure modes, and surface-tissue interactions.

4:20pm **PC+AS+BI+EM+NS+PB+SS-TuA7 Ambient Pressure X-Ray Photoelectron Spectroscopy Studies of Catalytically Active Interfaces using Electron Transparent Graphene Membranes***, R. Mom, L. Frevel,* Fritz-Haber Institute of the Max Planck Society, Germany*; J.J. Velasco-Velez,* MPI CEC Mülheim, Germany*; T.E. Jones, M. Plodinec,* Fritz-Haber Institute of the Max Planck Society, Germany*; R. Schlögl,* MPI CEC Mülheim, Germany*; **Axel Knop-Gericke**,* Fritz Haber Institute of the Max Planck Society, Germany **INVITED**

Green production of hydrogen will be an important building block in the transition to a carbon-balanced economy and could be realized by electrolytic water splitting powered by cheap renewable energy sources. Water electrolysis is currently limited by the oxygen evolution reaction (OER) and development of the associated catalysts is proceeding slowly, mainly due to missing descriptors for activity and stability of working OER catalysts. Herein, we contribute to that emerging field with in situ XPS and NEXAFS on iridium anodes. In our in situ cell the catalyst is probed through a graphene layer, which traps an electrolyte layer around the catalyst and provides electrical contact for separated iridium nanoparticles. In this way we enhance spectroscopic signal from the active surface relative to the bulk of the catalyst and reduce mass transport problems. In taking advantage of these benefits, we found that the two well-known oxidation waves occurring before the OER onset are connected to the development of two different types of electron deficient oxygen species, which are bound to one (μ_1) or two (μ_2) iridium atoms. It appears that oxygen is not only a “non-innocent ligand”, but rather a protagonist in the catalysis of the OER.

During the electrochemical reduction of oxygen, platinum catalysts are often (partially) oxidized. While these platinum oxides are thought to play a crucial role in fuel cell degradation, their nature remains unclear. We studied the electrochemical oxidation of Pt nanoparticles using in situ XPS. By sandwiching the particles between a graphene sheet and a proton exchange membrane that is wetted from the rear, a confined electrolyte layer was formed, allowing us to probe the catalyst under wet electrochemical conditions. We show that the behavior at the onset of Pt oxidation is influenced by the choice of proton exchange membrane, yet universally involves PtO_2 formation. The oxidation process is fast: even bulk oxide growth occurs on the sub-minute timescale. Thus, our observations indicate that PtO_2 may take part in the transient processes that dominate Pt electrode degradation.

5:00pm **PC+AS+BI+EM+NS+PB+SS-TuA9 The Influence of Density and Chemical Bonding on Atomic and Molecular Structures of Alcohols, Water and Oxides***, **Gabor A. Somorjai**,* University of California at Berkeley **INVITED**

Alcohol oxidation reaction over platinum nanoparticles with size ranging from 2 to 8 nm deposited on mesoporous silica MCF-17 was studied in the gas and liquid phases. Among methanol, ethanol, 2-propanol, and 2-butanol oxidations, the turnover frequency increased as the nanoparticle size became large in both reaction phases. The activation energy in the gas phase was higher than that in the liquid phase. Water co-adsorption decreased the turnover rate of all the gas and liquid phase oxidations except for the gas-phase 2-butanol case, while certain amount of water promoted 2-propanol oxidation in the liquid phase. Sum frequency generation vibrational spectroscopy (SFG) study and DFT calculation revealed that the alcohol molecules pack horizontally on the metal surface in low concentration and stand up in high concentration, which affects the dissociation of b-hydrogen of the alcohol as the critical step in alcohol oxidation.

Ice surfaces have water layers with thickness ranging from one monolayer at 100K to 30 layers of 273K. At the interfaces of two ice cubes, ice layers grow at the disappearing water interfaces (regelation). SFG studies of water surfaces show three peaks in the vibrational spectrum; “free OH^-”, liquid like hydrogen bonded water, with half bilayer termination, and ice-like water, with bilayer termination, with more hydrogen bonds.

Most nanocatalysts are composed of highly dispersed transition metal nanoparticles on oxides. The interface between the metal nanoparticles and the oxides plays a crucial role in determining the catalytic performance of nanocatalysts. Due to non-adiabatic electronic excitation, energetic electrons in metals can be generated during exothermic chemical processes. The energy barrier formed at the metal-oxide interfaces leads to the irreversible transport of energetic, or hot, electrons. The dopants and impurities present on the oxides can generate additional charge carriers or oxygen vacancies that affect the catalytic activity. The accumulations or depletion of hot electrons on the metal nanoparticles, in turn, can also influence the catalytic reactions. In this talk, we outline recent studies of the role of metal oxide interfaces and characteristics of fast charge transfer between metals and oxides that lead to ionization of molecules at the interface. The molecular ions produce so-called acid-base reactions. The electronic configuration of metal-oxide nanocatalysts during catalytic reactions will be introduced and its influence on heterogeneous catalysis will be outlined.

5:40pm **PC+AS+BI+EM+NS+PB+SS-TuA11 Atomic Scale Observation of Oxidation and Reduction of Palladium Surface**, ***Takehiro Tamaoka,*** *H. Yoshida, S. Takeda,* Osaka University, Japan

Reaction processes on metal surfaces under gas environment have been investigated in various research fields such as catalysis, gas sensing, and many more. Palladium is a well–known material which is used for hydrogen storage, hydrogen sensing, and exhaust catalysis. Therefore, the phase transition of palladium in hydrogen or oxygen has been extensively investigated by means of environmental transmission electron microscopy (ETEM). However, the oxidation and reduction process of palladium surface at the atomic scale remain poorly understood.

Here, we investigated the surface structure of a wedge–shaped palladium specimen in both hydrogen and oxygen by means of in-situ atomic resolution ETEM. Under ambient condition the surface of palladium is oxidized by several nanometers. After introducing hydrogen (100 Pa) in ETEM, the native oxide layer (PdO) was reduced to metallic fcc palladium even at room temperature. After exposure and exhaustion of hydrogen, we introduced oxygen (100 Pa) in ETEM. The palladium oxide was reproduced and the ETEM results show that the oxidation started from step edges and terraces and proceeded until the palladium surface was completely covered by the palladium oxide.

We also show that oxidation of palladium is dependent on the history of hydrogen exposure. When the duration of hydrogen exposure was over 90 min., we found that the surface was not oxidized. This was not due to bulk hydrogenation as demonstrated by our electron energy loss spectroscopy (EELS) results. We performed similar studies for the surface of platinum in oxygen after prolonged hydrogen exposure. However in platinum, the oxidation of the surface was not suppressed. This suggests that the process for suppression of oxidation, after prolonged hydrogen exposure, exists for palladium and not for platinum.

From these results, we hypothesize possible processes that explain how the prolonged hydrogen exposure suppresses the oxidation of palladium surface. We will also present atomic-scale in-situ movies on the surface dynamics in palladium and platinum in various processing.

6:00pm **PC+AS+BI+EM+NS+PB+SS-TuA12 Polymorphism of Hydrogen-Bonded Clusters at the Vacuum-Solid Interface**, ***Angela Silski,*** *J. Petersen,* University of Notre Dame*; R.D. Brown,* Clarkson University*; S. Corcelli, S.A. Kandel,* University of Notre Dame

Molecular self-assembly is an attractive bottom-up approach to nanostructure fabrication. Using molecules as building blocks and carefully tuning the non-covalent intermolecular interactions, unique nanostructured architectures can be designed. Given the structure/function relationship on the nano- and meso-scale, this bottom-up approach to designing new architectures is critical in the careful design of novel materials with desired chemical properties. In this study, the role of hydrogen bond donor/acceptor position in metastable cluster formation is explored using scanning tunneling microscopy (STM) with complementary density functional theory (DFT) calculations. We observe a metastable cyclic pentamer for isatin (1H-indole-2,3-dione) with DFT providing support for a cyclic structure stabilized by both NH...O and CH...O hydrogen bonds between neighboring molecules. The CH...O hydrogen bond is made between the 7-position proton acting as the hydrogen bond donor and the 3-position carbonyl as the hydrogen bond acceptor, and calculations indicate that the isatin pentamer structure is 12 kJ/mol more stable than the dimer on the per molecule basis. To probe the importance of the CH...O hydrogen bond in stabilizing the isatin pentamer, we compare to isatin derivatives: we replace the 3-position carbonyl with a methyl group (3-methyl 2-oxindole), the 7-position proton with a fluorine (7-fluoroisatin), systematically move the location of the hydrogen bond donor/acceptor by one position, (phthalimide), and remove of the primary hydrogen bond donor (1,2-indandione and 1,3-indandione). We show that cyclic pentamer formation is either altered or precluded as a result of these substitutions. Additionally, the importance of CH...O bonding in forming isatin pentamers is supported by electrospray ionization mass spectrometry (ESI-MS) measurements, which include a magic-number isatin pentamer peak, whereas the derivative molecules show little clustering under the same conditions. This work is significant in understanding the role that the position of the hydrogen bond donor/acceptor groups has on the resulting 2D supramolecular assemblies.

Plasma Science and Technology Division

Room 104A - Session PS+EM+NS+SS-TuA

Plasma Processing of Challenging Materials - II

Moderators: Michael Gordon, University of California at Santa Barbara, Wei Tian, Applied Materials Inc.

2:20pm **PS+EM+NS+SS-TuA1 Self-limiting Growth of III-nitride Materials via Hollow-cathode Plasma-ALD: Structural and Chemical Analysis**, ***Necmi Biyikli,*** *A. Mohammad, D. Shukla,* University of Connecticut **INVITED**

Plasma-assisted/enhanced atomic layer deposition (PALD) provides an alternative route for the low-temperature synthesis of III-nitride thin films with sub-monolayer precision thickness control, ultimate three-dimensional conformality, and large-area uniformity. On the other hand, PALD synthesis of AlN, GaN, and InN films required relatively long plasma co-reactant exposure durations (40 - 120 sec) to achieve self-limiting surface saturation with minimal carbon impurities which directly correlates the effectiveness of the ligand-removal process. During such extensive plasma half-cycles, the plasma source itself is exposed to elevated temperatures and along with energetic hydrogen radicals, which resulted in etching of conventional quartz-based inductively coupled plasma (ICP) sources. We have mitigated this problem by using a stainless-steel based capacitively-coupled hollow-cathode plasma (HCP) source, which reduced the oxygen impurity levels at least two orders of magnitude in GaN films while increasing the average film grain/crystallite size of AlN films by one order of magnitude.

Using HCP-assisted ALD (HCP-ALD), we have grown the entire III-nitride wide bandgap semiconductor family (AlN, GaN, InN) at ≤200°C substrate temperatures with single-phase hexagonal poly-crystalline material quality. However, there is still plenty of room and need for improvement in material properties before we can use these layers as active device layers. A careful systematic study needs to be carried out to achieve device quality III-nitride films via HCP-ALD. In this talk, we will present an overview of our HCP-ALD efforts including our recent materials characterization results obtained with a custom-design HCP-ALD reactor. A particular focus will be devoted to the structural and chemical properties of the III-nitride films and how they correlate with reactor parameters and plasma conditions.

3:00pm **PS+EM+NS+SS-TuA3 Electrostatic Charge of Solution-droplet in Plasma-coupled Micro Reactor**, ***Tae Hwan Kim,*** *SW. Lee,* National Fusion Research Institute, Republic of Korea

Plasma-liquid interaction research has increased because of emerging technological applications such as material synthesis, plasma bio-applications, environmental applications, and agriculture/food applications. Recently, an important scientific breakthrough in the understanding of the liquid reaction at the plasma-liquid interface that an electron transfer reaction at the plasma-liquid interface that leads to electrochemical reactions, which is referred to as the plasma electrochemical reaction [1]. Further evidence of plasma electron reaction (PER) was observed that the electrons in plasma can be solvated in a plasma electrochemical system [2].

In this talk, we present a new reaction pathway in which plasma-liquid interaction can cause an electrostatic charge in a liquid and the electrostatically charged solution can produce an electrochemical reaction. The experiments were performed with our newly designed plasma-coupled-microreactor (PCM), which can control the ambient gas and initiate a rapid plasma electrochemical reaction. Helium(He)-droplets and liquid-droplets were formed, and microplasma-droplets were ignited by dielectric barrier discharge (DBD). The generated microplasma-droplet can induce not only PER but also an electrostatic charge in a solution. The charge of the solution by microplasma-droplet and liquid-droplet interaction can be affected by the type and amount of stabilizer, the acidity of the solution, and the length of the electrodes used to form microplasma-droplets.

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[2] P. Rumbach, David M. Bartels, R. Mohan Sankaran, David B. Go, The solvation of electrons by an atmospheric-pressure plasma. Nat. Commun. 6, 7248 (2015).

3:20pm **PS+EM+NS+SS-TuA4 Surfactant-free and Stable Colloidal Metal Oxide Ultra-small Quantum Dots via Plasma-liquid Electrochemistry***,* ***Dillibabu Padmanaban****, D. Carolan, R. McGlynn, T. Velusamy, P. Maguire, D. Mariotti,* Nanotechnology & Integrated Bio-Engineering Centre, Ulster University, UK

Metal oxides are materials of great importance and interest with exceptional chemical stability, tunable optical and electrical properties and, importantly, meeting cost and environmental requirements for a sustainable future. For these reasons metal oxides nanoparticles are being investigated for a very wide range of applications that include energy harvesting and solar conversion and for exploiting nanoscale effects. However, due to synthesis challenges, the properties of ultra-small and quantum confined metal oxide nanoparticles, or quantum dots (QDs), are still very little understood while expected to offer exciting opportunities. Here we demonstrate that the synthesis of metal oxide QDs can be achieved by plasma-liquid electrochemistry with exceptional control of the size distribution even for particles well below 2 nm in diameter. Plasma-induced chemistry initiated at the plasma-liquid interface allows for rapid and simple production of highly stable colloidal suspension in ethanol of surfactant free metal oxide QDs, where a solid metal foil acts as the metal precursor. We provide an overview of these capabilities for a range of metal oxides that include Cu, Ni, Co, Mo and Zn oxides. We then study in detail the synthesis mechanisms leading to cupric oxide (CuO) QDs providing a range of experimental evidence that clarifies chemical reaction pathways due to the plasma interacting with ethanol. For a better understanding of the plasma chemistry, the process was also studied with different electrodes so to assess the impact of QDs formation in the overall plasma-ethanol chemistry. We have carried out extensive material characterization for the QDs and we have also analysed liquid products at different conditions by Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, nuclear magnetic resonance, mass-spectroscopy etc. Our work points at the role of different species in the synthesis of QDs. We believe that some of these chemical pathways may be general and applicable to the formation of other metal oxide QDs, however in some cases (e.g. for Mo-oxide) we expect some deviations. Overall our work discloses important general aspects of plasma-liquid interactions, in particular when ethanol is used. The study of the properties of our metal-oxide QDs uncovers quantum confinement effects that can become particularly useful in many application and suggest exciting opportunities in the control of defects and achieving phases that are difficult to produce with other methods.

4:20pm **PS+EM+NS+SS-TuA7 From Organometallic Precursors to Bimetallic Nanocatalysts using Atmospheric-pressure Plasma Processes***,* ***Joffrey Baneton****, J. Mertens, M. Smiljanic, S. Cauchies, T. Segato,* Université Libre de Bruxelles, Belgium*; Y. Busby,* Université de Namur, Belgium*; G. Caldarella,* Université de Liège, Belgium*; V. Debaille, S. Godet,* Université Libre de Bruxelles, Belgium*; J.-J. Pireaux,* Université de Namur, Belgium*; N. Job,* Université de Liège, Belgium*; M.J. Gordon,* University of California at Santa Barbara*; R.M. Sankaran,* Case Western Reserve University*; F. Reniers,* Université Libre de Bruxelles, Belgium

Developing new technologies to produce energy while respecting the environment is one of the important challenges in materials science. One of the possible routes is the use of hydrogen fuel cells. Unfortunately, some limitations remain such as the electrocatalysis of the reduction of dioxygen which requires a rare and expensive metal: platinum [1]. Therefore, minimizing its amount at the cathode while maximizing its accessibility, electroactivity and stability constitutes one of the main goal of current research. An interesting way consists in the synthesis of platinum-based alloys. Indeed, it is well known in the literature that combining two metals leads to the production of durable materials with higher activity [2].

Different routes can lead to the formation of bimetallic nanostructures including wet-chemistry, ultrasound processes or thermal evaporation. In this catalogue of methods, atmospheric-pressure plasma techniques are very attractive due to their versatility, rapidity and ease of use. In the present research, two different kinds of reactors, a microplasma device [3] and radio-frequency plasma torch [4], have been used to study the synthesis of bimetallic nanoparticles from acetylacetonate precursors. A complete chemical and morphological characterization is provided thanks to the combined use of X-ray photoelectron spectroscopy, transmission electron microscopy, UV-visible spectroscopy and X-ray crystallography.

Different experimental parameters can play a crucial role is the reduction process of the organometallic precursors. For example, concerning the microplasma system, the initial concentrations have a direct influence on the size distribution and agglomeration while, concerning the RF plasma torch treatment, the nature of the plasma gas mixture can limit the production of nanoparticles or favor their anchoring at the surface of a carbon support [5]. After optimization of the processes, electrochemical measurements were conducted to evaluate their activity, stability and performances as catalysts for hydrogen fuel cells.

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[4] D. Merche et al. Plasma Process. Polym. (**2016**), 13, 91–104.

[5] A. Felten et al. J. Phys. D: Appl. Phys. (**2007**), 40, 7379.

4:40pm **PS+EM+NS+SS-TuA8 Synthesis of Hydrogenated Amorphous Carbon Nanoparticles using High-Pressure CH_4+Ar Plasmas and Their Deposition***,* ***Kazunori Koga****, S.H. Hwang, K. Kamataki, N. Itagaki,* Kyushu University, Japan*; T. Nakatani,* Okayama University of Science, Japan*; M. Shiratani,* Kyushu University, Japan

Nanostructure fabrication such as nanoparticles through bottom-up processes is important in nanotechnologies due to their size-related properties [1]. Plasma is a powerful tool to produce nanoparticles. To control their size, pulsed discharge plasmas are commonly employed, but the plasmas have the limitation of the throughput. To realize continuous production, we have developed a multi-hollow discharge plasma chemical vapor deposition (MHDPCVD) method. We have succeeded in producing crystalline Si nanoparticles of 2 nm in size using hydrogen diluted silane plasmas [2, 3]. Here we applied the method to synthesis carbon nanoparticles. The experiments are carried out by CH_4+Ar MHDPCVD. CH_4 and Ar were injected into the reactor, flowed through hollows of 5 mm in diameter in the electrode. The gas flow rate ratio of CH_4 and Ar was 1:6. The total gas flow rate was 10 to 200 sccm . The pressure was kept at 2 Torr. Discharges were generated in hollows by applying rf power of 40 W at 13.56 MHz. Nanoparticles are nucleated and grow in the discharges. They are transported outside of the discharges by the fast gas flow and the growth of the nanoparticles are stopped. They deposited on TEM mesh grids set on the substrate holder 50 mm far from the electrode. From TEM measurements, spherical nanoparticles were deposited on the grid. The mean size decreases from 270 nm for 10 sccm to 20 nm for 120 sccm . The gas residence time for 120 sccm is 1/12 of that for 10 sccm . The size for 120 sccm is 1/13.5 of that for 10 sccm . The results indicate that the size of carbon nanoparticles are controlled by gas residence time of nanoparticles in plasmas. Above 125 sccm, No nanoparticle is observed on the TEM mesh. It suggests that deposition of nanoparticles depends on gas flow velocity and direction on the substrate.

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[2] T. Kakeya, et al., Thin Solid Films 506 (2006) 288.

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5:00pm **PS+EM+NS+SS-TuA9 Antimony-doped Tin Oxide Nanocrystals Synthesized by Low Temperature Plasma***, **Qinyi Chen**, E. Thimsen,* Washington University in St. Louis

For electrochemical applications, metal-oxide materials are attractive as electrodes for reactions occurring at positive potentials in the presence of water. Often, these metal-oxide materials function as an electrically-conductive support for a noble metal catalyst, and therefore must have very high specific surface area. Among conductive metal-oxide materials, antimony-doped tin oxide (ATO) stands out with its combination of: 1) high chemical stability over a wide range of pH values and reduction potentials, 2) high electrical conductivity, and 3) abundant constituent elements. Synthesis of ATO nanocrystals has been developed in liquid phase using sol-gel and colloidal methods. However, post-synthesis heat treatments are required to activate the electron donors and increase the conductivity of ATO nanocrystal assemblies prepared using liquid-phase techniques, which may adversely affect the surface area and pore structure of the material. In this work, we report on our efforts to synthesize monodispersed, conductive ATO nanocrystals through a single-step low temperature plasma growth method without any post treatments. Precursor vapors of tin and antimony were fed into a radiofrequency, flow-through low temperature plasma reactor. The precursor vapors reacted to nucleate ATO nanocrystals. Thin films comprised of ATO nanocrystals were then immediately deposited by supersonic impact deposition of the aerosol resulting from plasma synthesis. The resulting materials were characterized by a variety of methods to determine film thickness, porosity, nanocrystal size, and elemental composition. Local electron concentration and mobility within the nanocrystals were assessed by Fourier-transform infrared absorption spectroscopy. Hall effect was used to characterize longitudinal electrical transport in the film. The nanocrystal growth mechanism in the plasma will be discussed with a focus on antimony dopant incorporation. The effects of nanocrystal size on the transport properties of ATO thin films will be presented.

5:20pm **PS+EM+NS+SS-TuA10 Femtosecond Laser Texturing of Plasma-immersed Ti to Create TiN***, **Chisung Ahn**, E. Barlaz, D.N. Ruzic,* University of Illinois at Urbana-Champaign

Pulsed femtosecond lasers have been used as a functionalization method for metal surfaces due to their ability to produce nanostructures uniformly with easily controlled user inputs such as spot size and exposure repetition. Laser assisted nitriding of Ti in ambient nitrogen has previously been demonstrated in our group to significantly reduce native oxides. A major challenge to the current process is the limited ability of the laser to produce nitrogen radicals.

In this study, we investigate the effects of increased nitrogen radical concentration on surface topography and chemical composition for textured Ti metal. A secondary DC plasma is generated along the path length of the laser close to the sample surface in ambient nitrogen and under vacuum. The surface topography and chemical compositions of the resultant Ti coupons are analyzed by SEM and XPS respectively. Changes to hydrophilicity are quantified using contact angle measurements.

5:40pm **PS+EM+NS+SS-TuA11 Modeling Chemical Reactions in Contact Glow Discharge Electrolysis***, **Bocong Zheng**, M. Shrestha, K.L. Wang, T. Schuelke, Q.H. Fan,* Michigan State University

Contact glow discharge electrolysis is becoming attractive for nanomaterials manufacturing and surface engineering. In this discharge electrolysis, an electrode is submerged in a liquid electrolyte and a plasma is formed in a vapor layer around the electrode. The process combines the characteristics of electrolysis and plasma discharges, creating high-energy-density plasmas that lead to intensive physical processes and chemical reactions on the working electrode. The authors have found that the physical processes and the chemical reactions could be decoupled under certain conditions. In that case, a textured electrode surface could be created through a chemical-reaction-dominated process instead of an irregular porous surface produced by the physical-reaction-dominated interactions. The mechanisms are not clearly understood yet. This study aims to elucidate the plasma characteristics and the chemical reactions in contact glow plasma electrolysis. A plasma fluid model is established to predict the discharge process with constraint conditions obtained from the experiments. The modeling reveals that the plasma is highly electronegative, and the dominant neutral species are H_2 and O_2 dissociated from water vapor. The formation of textured surface is attributed to the anisotropic chemical etching by the reactive species generated in the plasmas.

6:00pm **PS+EM+NS+SS-TuA12 Effects of Light Ion Beam Irradiation in Plasma Etching Processes***, **Kazuhiro Karahashi**, T. Ito, H. Li, M. Isobe, K. Mizotani, S. Shigeno,* Osaka University, Japan*; M. Fukasawa, A. Hirata, T. Tatsumi,* Sony Semiconductor Solutions Corporation, Japan*; S. Hamaguch,* Osaka University, Japan

Gases containing hydrogen are widely used in microfabrication processes of electronic devices using plasma etching. For example, HBr gas is used for silicon etching, hydrofluorocarbon gases are used for silicon oxide etching, and Hydrocarbon-based non-corrosive gases are used for transparent conducing oxides etching. Unlike other atoms, hydrogen is lighter in weight, smaller in atomic radius, and chemically reactive, so it has various effects in the etching process. In order to precisely control the etching reaction and realize nanometer order microfabrication processes, it is necessary to clarify the effect of hydrogen. In this study, by comparing various effects on etching processes between hydrogen and helium incident ions using molecular dynamics (MD) simulation and ion beam experiments, physical and chemical effects by such light ion injection on etching processes were evaluated.

We have shown in this study based on MD simulation and ion beam experiments that, when a Si surface exposed to an O radical flux is simultaneously irradiated by an H^+ or He^+ ion beam, diffusion of oxygen atoms into the Si film is promoted. Since the enhanced diffusion occurs in a similar manner in both cases of H^+ and He^+ ion injections, it is clear that the enhanced diffusion is essentially caused by knock-on effects by incident light ions. On the other hand, in the case of etching of ZnO, which is an ionic crystal, our beam experiments have shown that its crystal size decreases by light ion irradiation using in-plane X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) measurements. The reduction of grain sizes seems correlated with the reduction of the physical sputtering yield of the ZnO film.

The results above show the following two physical effects by irradiation of a substrate with light ions such as H^+ and He^+ ;1) enhancement of diffusion of heavy atoms deposited on the substrate surface into it's the bulk of the film and 2) decrease of grain sized of ionic crystalline substrate due to amorphization and recrystallization. The decrease of grain sizes, which induce the increase in grain boundary areas may contribute to an increase in sputtering yield of the substrate.

Plasma Science and Technology Division
Room 104C - Session PS+PB+SE-TuA

Atmospheric Pressure Plasmas

Moderators: Francois Reniers, Université Libre de Bruxelles, Steven Vitale, MIT Lincoln Laboratory

2:20pm **PS+PB+SE-TuA1 Compact, Low Cost Atmospheric Pressure Plasma Jets Driven by Piezoelectric Transformers***, **Michael Johnson**,* National Research Council*; D.R. Boris, L. Petrova, S.G. Walton,* Naval Research Laboratory

In order for non-thermal atmospheric pressure plasma technology to be used for applications outside of the laboratory, there is a need to develop low-cost, portable devices that can be used for applications in the field. Constructing portable power supplies that can produce stable, non-thermal plasmas in full density air can be challenging as large electric fields are required to generate breakdown. Piezoelectric transformers are solid state transformers that can produce large gains in voltage, which makes them attractive candidates for plasma production. In this work, a piezoelectric transformer is used to amplify a low voltage AC signal in order to produce an atmospheric pressure plasma jet. Using this approach, plasma jets were generated with input voltages as low as 10 V when the piezoelectric transformer was operated at its resonance frequency (≈ 88 kHz). The electrical and optical characteristics of the piezoelectric driven plasma jet was compared to a plasma jet produced using a conventional high voltage sinewave of comparable operating frequency. Both jets were examined in helium and argon for a variety of different flow rates and operating voltages. The length of the jets were measured to determine if the piezoelectric transformer limited the potential size of the plasma jet. The current carried by the plasma jets were measured along with optical emission spectroscopy to examine the relative characteristics of the jets. Together, the results suggest the piezoelectric material may have influence beyond simple voltage amplification.

This work was supported by the Naval Research Laboratory Base Program. This research was performed while Michael Johnson held an NRC Research Associateship award at the U.S. Naval Research Laboratory.

2:40pm **PS+PB+SE-TuA2 Process Regimes of Atmospheric Pressure Plasma-enhanced Chemical Vapor Deposition with Source Materials Highly Diluted in Inert Gases***, **SeungJae Baik**, J. Jang,* Hankyong National University, Republic of Korea*; H.-J. Oh,* Yonsei University, Republic of Korea

Plasma-enhanced chemical vapor deposition (CVD) is appropriate for fast deposition with moderate film quality, but to form high quality materials such as epitaxial thin films, thermal processes at higher temperature are more favorable. High energy particles that are statistically produced in plasma processes are sources of film quality degradation. It has been previously reported that the plasma process at high working pressure, e.g., atmospheric pressure is feasible for epitaxial Si growth; where source gas species are highly diluted in inert gas. Employing a large dilution of source materials opens a new process regime in plasma-enhanced CVD: (1) low damage plasma processing (2) high deposition rate process with controlled powder generation (3) efficient usage of source materials.

We have performed Si thin film deposition processes with silane and hydrogen as source materials highly diluted in He or Ar gases under working pressure close to the atmospheric pressure (up to 700 torr). The new process regimes showing low damage plasma processing, high deposition rate with controlled powder generation, and efficient usage of source materials are experimentally demonstrated in various process conditions. In addition, the impurity incorporation into the film during deposition processes degrades the crytalline quality of the deposited Si thin films, which can be improved by employing plasma electrode pre-coating or pre-deposition cleaning process. Furthermore, the trade-off relation of plasma power and gas flow velocity revealed the process window of polycrystalline thin film deposition, and even epitaxial growth.

Atmospheric plasma-enhanced CVD tool is promising for fast deposition and low damage processing, and moreover, cheaper setup may also be viable via pre-deposition cleaning processes instead of utilizing expensive vacuum facilities.

3:00pm **PS+PB+SE-TuA3 Plasma-enhanced Chemical Film Conversion (PECFC): Direct, Low-temperature Growth of Solution-processible and Printable Layered Thin Films***, T. Liu, **R. Mohan Sankaran**,* Case Western Reserve University

In plasma-enhanced chemical vapor deposition (PECVD) and plasma-enhanced atomic layer deposition (PEALD), the addition of a plasma to dissociate or excite the gas molecules and create active chemical and energetic species can lower the thermal energy required at the substrate to drive thin film nucleation and growth. Here, we show that a similar approach can be used to lower the temperature required to convert molecular precursors deposited from solution onto a substrate to a functional, crystalline thin film which we term plasma-enhanced chemical film conversion (PECFC). We apply this method to layered materials such as hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS_2) whose applications are currently limited by the lack of large-area, low-temperature, direct (substrate independent) growth processes.

Our experimental setup consists of an atmospheric-pressure, planar, dielectric barrier discharge and a cold wall substrate heater. Single molecular precursors for h-BN, ammonia borane, or MoS_2, ammonia tetrathiomolybdate were dissolved in solution and deposited by a variety of methods including dropcasting, airbrush spraying, spin coating, and inkjet printing on different substrates such as silicon (Si), silicon dioxide (SiO_2), and copper. The area of the film was only limited by the current size of our plasma source which is ~2 in^2. After conversion, the films were characterized by X-ray diffraction, micro Raman spectroscopy, atomic force microscopy, scanning electron microscopy, and transmission electron microscopy. We systematically compared thermal and plasma-assisted conversion at the same temperatures, background gas environments, and substrates. For h-BN, our results show that thermal conversion requires a minimum of 800 °C to nucleate on SiO_2, but only 650 °C with the addition of a plasma. Adding 20% H_2 enables a further 150 °C reduction for plasma conversion. For MoS_2, our results show that nucleation is enhanced in the presence of a plasma at the same growth temperature of 500 °C and a subsequent annealing step leads to a smooth (<0.2 nm RMS surface roughness) and highly crystalline film. We suggest that plasma species, especially atomic hydrogen (H), are involved in several important surface reaction mechanisms including abstraction of hydrogen, insertion in strained bonds, and radical formation, to enhance grain growth that overall enhance nucleation and growth of crystalline domains. We will also discuss the performance of the PECFC materials in electronic and energy devices.

3:20pm **PS+PB+SE-TuA4 Plasma-based Remediation of Nanoscale Particulate Matter in Charbroiler Smoke Emissions***, **Sisi Yang**, S. Subramanian,* University of Southern California, Los Angeles*; D. Singleton,* Transient Plasma Systems*; C. Schroeder, W. Schroeder, M. Gundersen, S.B. Cronin,* University of Southern California, Los Angeles

Recent studies have shown ultrafine particulate matter (UFPM) produced in commercial charbroiling processes represents a serious health hazard and has been linked to various forms of cancer. In this study, we demonstrate a highly effective method for treating restaurant smoke emissions using a transient pulsed plasma reactor based on a nanosecond high voltage pulse generator. We measure the size and relative mass distribution of particulate matter produced in commercial charbroiling processes (e.g., cooking of hamburger meat) both with and without the plasma treatment. Here, the plasma discharge is produced in a 3" diameter cylindrical reactor with a 5-10 nanosecond high voltage (17 kV) pulse generator. The distribution of untreated nanoparticle sizes peaked around 125-150 nm in diameter, as measured using a scanning mobility particle sizer (SMPS) spectrometer. With plasma treatment, we observe up to a 55-fold reduction in total particle mass and a significant reduction in the nanoparticle size distribution using this method. The effectiveness of the UFPM remediation increases with both the pulse repetition rate and pulse voltage, demonstrating the scalability of this approach for treating higher flow rates and larger systems.

4:20pm **PS+PB+SE-TuA7 The Interactions of Atmospheric Pressure Plasma Jets with Surfaces: *In situ* Measurements of Electron Heating in Materials***, **Scott Walton**,* U.S. Naval Research Laboratory*; J. Tomko, B.M. Foley,* University of Virginia*; D.R. Boris,* U.S. Naval Research Laboratory*; M.J. Johnson,* National Research Council*; Tz.B. Petrova,* U.S. Naval Research Laboratory*; A. Giri, P.E. Hopkins,* University of Virginia

The energy flux to a surface during plasma exposure and the associated surface heating are of long standing interest since both contribute to the physicochemical changes during plasma-based materials processing. A unique feature of plasmas compared to other methods of materials synthesis and processing is that the energy flux is delivered and absorbed at or very near the surface over short time scales, and thus requires fast, surface-sensitive techniques to fully appreciate the dynamics of the plasma-surface interface. To achieve this, we employ pump-probe Time-Domain Thermoreflectance (TDTR) to measure electron and phonon excitation and energy transport dynamics in thin metal films during exposure to an atmospheric pressure plasma jet. The results show the energy delivered by the plasma jet causes a localized thermal spike that is dissipated radially from the point of contact. More specifically, energy delivered via the flux of particles and photons causes the kinetic energy of the electrons within the material to increase over an area commensurate with the plasma jet radius. That energy is then dissipated through electron-electron collisions and electron-phonon interactions as the electrons propagate radially from the point of contact. These results, in conjunction with voltage and current measurements, will be discussed in an effort to develop a first order understanding of energy transfer and relevant kinetics during plasma jet–surface interactions. This work is partially supported by the Naval Research Laboratory base program.

4:40pm **PS+PB+SE-TuA8 Surface Activation by Atmospheric Plasma: the Right Technology for the Right Application***, A. Ozkan, D. Merche, **Francois Reniers**,* Université Libre de Bruxelles, Belgium

Cold atmospheric plasma are widely used for surface activation in many applications. Today, many technologies are available, such as coronas, dielectric barrier discharges (DBDs), remote (or post-discharge) DBDs, torches, operating in the radiofrequency mode, gliding arcs, ……. A wide variety of operating conditions can be found in the literature or on the websites of the manufacturers : AC, DC, kHz range, noble gas or air, high or low power, ….. For the scientist, the lab manager, or the CTO of a company looking for a new, clean, activation technique, the vast list of possibilities, although representing opportunities, may represent a challenge. In this paper, we try to set up a product driven roadmap to help the scientist making the best choice for the plasma technology to implement for his application. Through a few selected examples, all tested in our laboratory equipped with 7 different plasma technologies and 15 reactors, we show which is the best technology for the application of interest. Advantages and drawbacks of each of the tested technologies with respect of the material, the energy consumption, and the time and cost of operation are presented, and discussed in terms of plasma and surface characterization.

The applications chosen addresses a wide range of questions such as:

- which plasma to chose to clean and activate glass substrates (a comparison between torches and in-situ DBDs is proposed)

- atmospheric plasma to grow an oxide layer on aluminium : a comparison between an air operated torch and plasma electrolytic oxidation

- how to activate a macroscopic 3D pre-painted metal piece for further painting using an atmospheric plasma torch. A comparison between 4 torches is presented

- how to activate the surface of selected polymers using DBD, RF torches with different gases

- how to activate surfaces (silicon, polymers, nanotubes) for further grafting of metal nanoparticles

- how to modify PTFE using a torch, what are the side effects, and why.

These examples will be starting points for a more general discussion about methodology, based on the final expectations and the chemistry and physics of each technology.

5:00pm **PS+PB+SE-TuA9 Aluminum Alloy Surface Cleaning by Atmospheric Pressure Microwave Discharge***, **Lucia Bonova**, W. Zhu, A. Farrokhpanah, D.V. Krogstad, Z.K. Jeckell, S. Chaudhuri, D.N. Ruzic,* University of Illinois at Urbana-Champaign

Aluminum and its alloys are commonly used as lightweight materials in many industrial sectors including aerospace. During the manufacturing process of aluminum, a series of lubricants and additives are used to avoid sticking of layers and prevent degradation or corrosion. The residual hydrocarbon film is typically removed by a chemical chromate process prior to the deposition of an anticorrosive layer. We present an alternate method to remove the hydrocarbons deposited on the aluminum surface by an atmospheric pressure microwave discharge.

The Center for Plasma Material Interaction (CPMI) at University of Illinois has developed novel patented technologies of Evaporative Coatings at Atmosphere Pressure (ECAP) using a 2.45 GHz microwave power to treat the aluminum surface with an air plasma at atmospheric pressure. The cleaning effect of this microwave plasma was analyzed by contact angle measurements, XPS and ATR-FTIR.

5:20pm **PS+PB+SE-TuA10 Temporal and Spatial Study of a Parallel pin-plate Plasma Reactor***, **Vladimir Milosavljević**, M. Gulan, L. Scally, P.J. Cullen,* BioPlasma Research Group, Dublin Institute of Technology, Dublin, Ireland

Electrical discharges in gases have demonstrated a wide range of effects for material science and energy applications. Under both laboratory and industrial setups, such electrical discharges can produce a stable plasma. From both fundamental and applied purposes, such gaseous plasmas are well studied, the technology has found many applications. Recent interest has turned to operating such plasma under atmospheric conditions. The main advantage of the plasma discharge at atmospheric pressure over low-pressure plasma or high-pressure plasma, is that no reaction vessel is needed. However, with increasing gas pressures, the stability and reproducibility of the plasma discharge are significantly impacted. For atmospheric pressure, in order to obtain a stable plasma discharge in addition to the electrodes a dielectric barrier is required. The function of this dielectric is to spread the electrical charge throughout the entire electrode in order to create multiple conducting paths for the discharges to occur. This is the foundation of the Dielectric-barrier discharge (DBD). One or both electrodes in DBD could be covered by a dielectric material which serves as an electric polarizer, and helps maintain a low gas temperature. Over the course of its life, for any DBD system, the biggest disadvantage is the dielectric contamination. In most cases, this dielectric is a polymer, and polymers are generally fragile materials. Therefore, developing a plasma system that does not require a dielectric, and has a reproducible and stable electrical discharge at atmospheric pressure would offer new system designs and applications.

This work presents a pulsing plasma system (PPS) which can run at atmospheric pressure under various external parameters. The system has a planar configuration with a bottom (grounded) flat electrode and a top multiple pin electrode (high voltage). The design of this PPS allows several parameters to be modified, such as: discharge frequency (30-125 kHz), duty cycle (1-100%), duty cycle frequency (100-3000 Hz), peak-to-peak voltage (up 60 kV), power (up to 700 W), distance between electrodes (up to 55mm), and treatment time (unlimited). The new plasma system allows an increase in the surface-plasma interaction selectivity and to reduce plasma induced damages to surfaces. The electron properties and gas radical density generated for the system under such control parameters are reported.

This work was funded by the Dublin Institute of Technology and PlasmaLeap Technologies, Ireland.

5:40pm **PS+PB+SE-TuA11 Plasma-modulated Metamaterials and Photonic Crystals***, **Jeffrey Hopwood**, H. Kim,* Tufts University

Metamaterials are periodic assemblies of man-made structures that can mimic naturally occurring materials. By clever design, electromagnetic transmission through metamaterials may have extraordinary properties such as negative refractive index. In this paper we describe the formation of atmospheric pressure argon microplasmas within metamaterials as well as photonic crystals. Microplasma ignition within these materials is initiated by first creating an implicit microwave or millimeter wave resonance within the structure. For example, a vacancy in the artificial crystalline structure can act as a millimeter wave cavity. Incident EM waves excite this resonance and the strong resonant electric field causes gas breakdown.

In general, metamaterials are pre-configured during the design process and exhibit fixed transmission characteristics. The self-initiated plasma, however, dynamically changes the metamaterial. We show that depending on the gas pressure and electron density, microplasma inclusions may act as dielectrics or conductors. Experimentally one observes that the appearance of microplasma causes a change in the material from transparent to reflective, or vice versa. A metamaterial consisting of an array of copper split-ring resonators (3x3x9) is described in terms of the plasma density and its microwave transmission from 1-3 GHz. The appearance of microplasmas quenches the resonance and decouples the resonators from one another; the transmission spectra are radically changed upon de-coupling. In the millimeter wave band, a photonic crystal consisting of alumina rods is shown to support argon plasma at 43 GHz. The transient response of the photonic crystal during pulsed EM radiation and plasma formation is measured and found to act as a power limiting device.

6:00pm **PS+PB+SE-TuA12 Generation of Large-Volume Transient Glow Discharge Plasma by an External Fast Ionization Wave (FIW) from a Plasma Jet***, **Hamid Razavi**, M. Laroussi,* Old Dominion University

A non-thermal transient glow discharge can be generated remotely in a nonconductive low–pressure chamber by an external guided fast ionization wave (FIW). We used an atmospheric-pressure LTP jet (APLTPJ) as an external source of FIW to transfer the enhanced electric field at the wavefront to a reduced–pressure Pyrex glass chamber with no electrical connection to the chamber [1]. Here, we study on the interaction of FIW with a dielectric surface which forms the wall of the low-pressure system.

In this study, key characteristics of the transient diffuse plasma are discussed. Plasma parameters were measured by Langmuir probe and APLTPJ electrical measurements were done to elucidate the operational mechanisms of the FIW as an igniter of a reduced pressure glow discharge plasma. It is shown that the transient discharge in the low-pressure chamber generates a bulk plasma with negative potential due to the nonconductive boundary. We also used Optical emission spectroscopy (OES) to show the physical and chemical characteristics of the APLTPJ plasma and the transient glow discharge plasma. It is shown that the glow discharge plasma is capable of producing second and third ionized nitrogen and oxygen atoms (OII, NII, and NIII). Fast images were taken by an intensified CCD to study the launching and propagation phases of both APLTPJ plasma and the transient reduced pressure glow discharge plasma as well as the incidence of the guided FIW on a dielectric surface.

[1] M. Laroussi and H. Razavi, “Indirect Generation of a Large Volume Diffuse Plasma By an Ionization Wave from a Plasma Jet”, *IEEE Trans. Plasma Sci*., Vol. 43, No. 7, pp. 2226-2229, (2015).

Reconfigurable Materials and Devices for Neuromorphic Computing Focus Topic

Room 203A - Session RM+EM+NS-TuA

IoT Session: Reconfigurable Materials and Devices for Neuromorphic Computing

Moderator: Brian Hoskins, National Institute of Standards and Technology (NIST)

2:20pm **RM+EM+NS-TuA1 Non-volatile Memories for Neuromorphic Computing*, Alec Talin,*** Sandia National Laboratories **INVITED**

Inspired by the efficiency of the brain, CMOS-based neural architectures and memristors are being developed for pattern recognition and machine learning. However, the volatility, design complexity and high supply voltages for CMOS architectures, and the stochastic and energy-costly switching of memristors complicate the path to achieve the interconnectivity, information density, and energy efficiency of the brain using either approach. In my talk, I will review the latest advances in neuromorphic computing architectures based on deep neural networks implemented using CMOS and memristors and describe the challenges in achieving both high accuracy and energy efficiency using these devices. I will then discuss an alternative approach based on the non-volatile redox memory (NVRM): a device with a resistance switching mechanism fundamentally different from existing memristors, involving the reversible, electrochemical reduction/oxidation of a material to tune its electronic conductivity. The first type of NVRM that I will describe is based upon the intercalation of Li-ion dopants into a channel of $Li_{1-x}CoO_2$. This Li-ion synaptic transistor for analog computing (LISTA) switches at low voltage (mVs) and energy, displays hundreds of distinct, non-volatile conductance states within a 1V range, and achieves high classification accuracy when implemented in neural network simulations[1]. The second type of NVRM I will describe operates on a similar principle but is based on the polymer system PEDOT:PSS, and which we call the electrochemical neuromorphic organic device (ENODe) [2]. Plastic ENODes are fabricated on flexible substrates enabling the integration of neuromorphic functionality in stretchable electronic systems. Mechanical flexibility makes ENODes compatible with three-dimensional architectures, opening a path towards extreme interconnectivity comparable to the human brain.

1) E. J. Fuller et al., Advanced Materials 29, 1604310 2017.

(2) Y. B. van de Burgt et al., Nature Materials 16, 414 2017.

(3) S. Agarwal et al., IEEE 2017 Symposium on VLSI Technology Digest of Technical Papers, DOI: 10.23919/VLSIT.2017.7998164.

4:20pm **RM+EM+NS-TuA7 Memristor Neural Networks for Brain-Inspired Computing*, Qiangfei Xia,*** University of Massachusetts Amherst **INVITED**

As CMOS scaling approaches its limits, it becomes more difficult to keep improving the speed-energy efficiency of traditional digital processors. To address this issue, computing systems augmented with emerging devices particularly memristors, offer an attractive solution. Memristors use conductance to represent analog or digital information. The dynamic nature of memristor with both long-term and short-term memories, together with its small effective size contributes to the energy efficiency in weight updating (training). The in-memory computing scheme in a crossbar breaks the ‘von Neumann bottleneck’ as the weights are stored locally in each device during computing. The read out (inference) is finished in one clock cycle regardless of the array size, offering massive parallelism and hence high throughput. The capability of using physical laws for computing in a crossbar enables direct interfacing with analog signals from sensors without energy- hungry analog/digital conversions.

We developed a Ta/hafnium oxide memristor with stable multilevel resistance, linear current voltage characteristics in chosen conductance ranges, in addition to high endurance and long retention. We further integrated the memristors with foundry-made transistors into large arrays. We demonstrated that the reconfigurable memristor networks are capable of analog vector matrix multiplication, and successfully implemented a number of important applications including signal processing, image compression and convolutional filtering. We also built a multilayer memristor neural network, with which we demonstrated in-situ and self-adaptive learning capability with the MNIST handwritten digit dataset. The successful demonstration of analog computing and in-situ online training suggests that the memristor neural network is a promising hardware technology for future computing.

5:00pm **RM+EM+NS-TuA9 Indium Phosphide Synaptic Device on Silicon for Scalable Neuromorphic Computing*, Jun Tao,*** *D. Sarkar, R. Kapadia,* University of Southern California

Inspired by the superior capability of the brain, neuronal spiking, and synaptic behavior have been mimicked by the CMOS-based neuronal cell in hardware, which contains 6-12 transistors depending on specific functionality and the robustness of the design. However, the higher energy consumption and physical area have led researchers to look for architectures based on single device and novel materials.

In our work, utilizing thin-film vapor-liquid-solid growth method, we fabricated scalable Indium phosphide (InP) channel transistors directly on Si/SiO_2 wafer, which can emulate significant synaptic characteristics such as elasticity, short- and long-term plasticity, metaplasticity, spike number dependent plasticity and spike timing dependent plasticity, by modeling gate electrode as the pre-synaptic axon terminal, the drain electrode as the post-synaptic dendrite, and the gate oxide-semiconductor channel as the synapse junction, in which we also interpreted the FET channel conductance as the synaptic weight.

We also demonstrated that by controlling the charging and discharging of interfacial traps at the gate oxide-semiconductor stack, we can essentially engineer hysteresis of the synaptic device to customize the synapse behavior and modify the synapse weight non-linearly. It underpins optimal selectivity of signal transduction and satisfies the key neuromorphic architecture characteristic—training and learn. Tuning hysteresis in a family of transfer characteristics in spike timing dependent plasticity (STDP) emulation, we attain maximum potentiation (depression) for the minimum positive (negative) interval time, which gradually decays down to elasticity, as we expected, indicating the scalable InP channel transistors on silicon as promising devices and platform for neuromorphic computation.

5:20pm **RM+EM+NS-TuA10 Ultra-low Power Microwave Oscillators based on Phase Change Oxides as Solid-State Neurons*, Boyang Zhao,*** *J. Ravichandran,* University of Southern California

Voltage or current controlled oscillators are well-established candidates for solid-state implementations of neurons. Metal to insulator transition (MIT) based phase change electrical oscillators are one of the many candidates for solid-state neurons, but current implementations are far from the ideal performance limits of energy and time necessary to induce the transition. We propose the use of nanoscale, epitaxial heterostructures of phase change oxides such as VO_2, NbO_2 and oxides with metallic conductivity as a fundamental unit of a low power electrical oscillator, capable of operating as neurons for neuromorphic computing architectures. Our simulations such that such oscillators can operate in the microwave regime and overcome many of the power consumption issues plagued by phase change electrical oscillators.

5:40pm **RM+EM+NS-TuA11 Leveraging Nanodevice Volatility for Low Energy Computing Inspired from Nature*, Alice Mizrahi,*** NIST/University of Maryland*; T. Hirtzlin,* Centre de Nanosciences et Nanotechnologies*; B. Hoskins,* NIST Center for Nanoscale Science and Technology*; A. Fukushima,* AIST*; A. Madhavan,* NIST Center for Nanoscale Science and Technology*; H. Kubota, S. Yuasa,* AIST*; N.B. Zhitenev, J. McClelland, M.D. Stiles,* NIST Center for Nanoscale Science and Technology*; D. Querlioz,* Centre de Nanosciences et Nanotechnologies, France*; J. Grollier,* UMR CNRS/Thales **INVITED**

Artificial neural networks are performing tasks, such as image recognition and classification, that were thought only accessible to the brain. However, these algorithms run on traditional computers and consume orders of magnitude more energy more than the brain does at the same task. One promising path to reduce the energy consumption is to build dedicated hardware to perform cognitive tasks. Nanodevices are particularly interesting because they allow for complex functionality with low energy consumption and small size. I discuss two nanodevices. First, I focus on stochastic magnetic tunnel junctions, which can emulate the spike trains emitted by neurons with a switching rate that can be controlled by an input. Networks of these tunnel junctions can be combined with CMOS circuitry to implement population coding to build low power computing systems capable of processing sensory input and controlling output behavior. Second, I turn to different nanodevices, memristors, to implement a different type of computation occurring in nature: swarm intelligence. A broad class of algorithms inspired by the behavior of swarms have been proven successful at solving optimization problems (for example an ant colony can solve a maze). Networks of memristors combined with CMOS circuitry can perform swarm intelligence and find the shortest paths in mazes. These results are striking illustrations of how matching the functionalities of nanodevices with relevant properties of natural systems open the way to low power hardware implementations of difficult computing problems.

Advanced Surface Engineering Division
Room 202C - Session SE-TuA

Wear, Oxidation and Corrosion Protective Coatings

Moderators: Suneel Kodambaka, University of California, Los Angeles, Andrey Voevodin, University of North Texas, Pantcho Stoyanov, Pratt & Whitney

2:20pm **SE-TuA1 Dissociative Extraction of Carbon-based Tribofilms from Hydrocarbon Molecules on Catalytically Active Nanocomposite Coatings***,* ***Ali Erdemir****, G. Ramirez, O.L. Eryilmaz,* Argonne National Laboratory **INVITED**

Diamondlike carbon (DLC) coatings are now used in large volumes to mitigate friction and wear-related problems in a wide range of moving mechanical assemblies [1]. In our laboratory, we have developed a class of new catalytically active nanocomposite coatings that can extract DLC type boundary films directly from the hydrocarbon molecules of lubricating oils and gas molecules and thus provide superior friction and wear properties. Specifically, these composite coatings are composed of catalytically active hard and soft nanophases affording exceptional catalytic responsiveness to the hydrocarbon molecules trapped at the sliding contact interface. When tested under lubricated sliding conditions, these coatings can crack or fragment hydrocarbon molecules and then deposit them on sliding surfaces as lubricious and highly protective boundary films. Using TEM, UV Raman and TOF-SIMS, we elucidated the structural chemistry of these boundary films and confirmed that they were indeed similar to conventional DLC films that are currently deposited using plasma-based CVD and PVD processes. TEM also confirmed the presence of graphene and carbon-nano-onions scattered within the tribofilm. Under severe sliding, reciprocating, and scuffing test conditions, these carbon-based boundary films showed extreme resistance to wear and scuffing [2].

[1] S-C. Cha and A. Erdemir, eds., “Coating Technology for Vehicle Applications” Springer, New York, 2015.

[2] A. Erdemir et al., Nature, 536(2016)67-71

3:00pm **SE-TuA3 Use of Carbon Nanotube-Silver Metal Matrix Composite Thin Films to Enhance Mechanical Properties of Grid Fingers and Busbars on Photovoltaic Cells***,* ***Cayla Nelson****,* University of New Mexico*; O.K. Abudayyeh,* Osazda Energy, LLC*; Y. Shen, S.M. Han,* University of New Mexico

The hot spots created by cell cracks have recently been identified as the most common degradation mode in PV modules.[1] Even before they become hot spots, these cracks lead to high series resistance, reduced efficiency, and lost energy. To reduce this degradation, we have been investigating the use of multiwalled carbon nanotubes (MW-CNTs) as a reinforcement in metal matrix composites. We have demonstrated that these composites provide gap-bridging capability (> 40 mm), “self-healing,” and fracture toughness against the cracks forming in the substrate and the metal contacts.[2-4] To accompany the experimental effort, finite element modeling (FEM) is used to relate the microstructure of the composite to its mechanical properties. The FEM models are compared to mechanical data taken by dynamic mechanical analysis (DMA). The composites are fabricated in a Ag/CNT/Ag layer-by-layer structure. The silver layer can be evaporated or electroplated, and the CNTs are spray-coated. The shape of the composite films is a dog bone structure that can be released from the substrate as a free-standing film. This release is necessary to extract the mechanical properties solely belonging to the composite. Fitting the FEM model to DMA measurements captures qualitative trends of how mechanical properties of the MMC change with CNT volume fraction. Combining mechanical modeling with experimental results provides predictive evaluation of CNT reinforced metal matrix composites.

[1] D. C. Jordan, T. J. Silverman, J. H. Wohlgemuth, S. R. Kurtz, and K. T. VanSant, "Photovoltaic failure and degradation modes," *Prog. Photovolt: Res. Appl.***25,** 318-326 (2017).

[2] O. Abudayyeh, N. D. Gapp, D. M. Wilt, and S. M. Han, "Methods to Mitigate Stress-Induced Metal Line Fractures for Thin-Film Solar Cells, Using Metal-Carbon-Nanotube Composites," Patent No. Application No. PCT/US2016/038197 (2016).

[3] O. K. Abudayyeh, G. K. Bradshaw, S. Whipple, D. M. Wilt, and S. M. Han, "Crack-Tolerant Metal Composites as Photovoltaic Gridlines," *Appl. Phys. Lett.***,** submitted (2018).

[4] O. K. Abudayyeh, N. D. Gapp, C. Nelson, D. M. Wilt, and S. M. Han, "Silver-Carbon-Nanotube Metal Matrix Composites for Metal Contacts on Space Photovoltaics," *IEEE J. Photovolt.***6,** 337-342 (2016).

3:20pm **SE-TuA4 Study of Effects of Synergistic Environmental Exposures on Fiber-Reinforce Polymer Composites Protected by Metallic Coatings***,* ***Arash Afshar****, D. Mihut, S. Hill,* Mercer University School of Engineering

Polymer composites are good candidates for applications requiring high strength, low weight and corrosion resistance properties. Therefore, they are widely being used in marine, automotive, construction, aerospace industries to name a few. However, the main existing challenge is preventing the degradation of composite materials under prolonged exposure to harsh environmental conditions such as UV radiation and moisture. Composite samples with standardized sizes were exposed to combined UV radiation and moisture in the environmental chamber for different time intervals. Some samples were coated with optically thick metallic materials using high vacuum magnetron sputtering deposition and were later exposed to the same combined environmental conditions. It was observed that metallic coatings improved the surface resistance of the substrate composite materials and protected the mechanical properties throughout the course of exposure. The surface morphology of samples before and after exposure was observed using optical microscopy and the adhesion of metallic layers to the substrates was examined using scanning electron microscopy. The mechanical properties were also characterized using flexural and hardness tests over the exposure time.

4:20pm **SE-TuA7 Atomistic View of Mg Metal Corrosion Using *in-situ* cryo-XPS and *ab initio* Computation***,* ***Vaithiyalingam Shutthanandan****, A. Martinez, P.V. Sushko, A. Devaraj, E. Stevens, O.A. Marina, V. Joshi, S. Thevuthasan, V. Murugesan,* Pacific Northwest National Laboratory

Magnesium metal is potential candidate for high strength to weight ratio alloys with wide application in aerospace and automotive industries. However, poor corrosion resistance under ambient environmental conditions is the bottleneck for industrial deployment. Designing passivation layers and/or corrosion resistance alloys require fundamental understanding of the corrosion process. The traditional *ex-situ* spectroscopic measurements of polycrystalline metal surface with ubiquitous surface impurities provided indistinct view of the corrosion process. To clearly distinguish the mechanism and sequence of corrosion process, we employed *in-situ* cryo-based x-ray photoelectron spectroscopy (XPS) measurements on well-defined Mg-single crystal surfaces in combination with *ab initio* atomistic modelling studies. Mg (0001) surfaces were exposed to ambient water conditions (i.e. D_2O and 5 wt% NaCl+95 wt% D-$_2$O solution) and the subsequent interfacial reactions were studies through integrated experimental and theoretical approach. This study provides atomistic view of $Mg(OH)_2$ nucleation as main product of the corrosion process. Under salt conditions, the competitive nucleation process between $Mg(OH)_2$ and $MgCl_2$ were observed. High resolution helium ion microscopy images of the corroded surface show unique morphologies of nucleates including some well-defined faceted cubic crystals and micron size faceted ribbon like structures. By combining the energy requirements from computational modelling and the electronic states of corrosion products, the mechanism and sequence of corrosion process on Mg metal will be discussed.

4:40pm **SE-TuA8 Scratch Behavior and Modelling of Cu/Si(100) Thin Films Deposited by Modulated Pulsed Power Magnetron Sputtering***, D. Meng, Y.G. Li,* ***M.K. Lei****,* Dalian University of Technology, China

A series of copper films on Si(100) substrate were deposited using modulated pulsed power magnetron sputtering under different sputtering pressure from 0.11 to 0.70 Pa. The scratch behavior of copper films on Si(100) was evaluated by scratch adhesion test with the aid of finite element modelling. With the increase of pressure, the surface morphology becomes rougher and the pattern transforms from compact fine granular structure to coarse and crack visible columnar structure, and the surface morphology of scratch tracks transforms from no obvious delamination to vast delamination. At pressure of 0.11 Pa, no obvious delamination can be observed, while copper films begin to delaminate with the growing pressure at 0.3 Pa and above at a certain load. Critical loads Lc_1 to Lc_4 were employed to assess the adhesion behavior of soft copper films on hard Si(100), the main exhibiting characteristics were the periodical plastic deformation on the side of scratch tip and semi-circular characteristic behind the scratch tip which were mainly caused by plastic deformation in the stick-slip process. Finite element modeling was employed to analyze the stress and strain responses of scratch on copper films by mainly using the maximum principal stress σ_1 as a function of normal loads in stress concentration zone A, B and C. The location of the peak σ_1 migrates from zone B to C which are tensile as the normal load increases, while peak σ_1 in zone A is compressive. The directionality of σ_1 for zone B tilts mostly at an out-of-plane angle mostly about 15º and 90º which may be responsible for the interface failure between the film and substrate. Critical loads Lc_1 and Lc_2 are evaluated through the migration of peak σ_1 from zone B to C, while critical load Lc_3 is associated with stress accumulation in zone C and stress accumulation in zone A is responsible for critical load Lc_4. The observed plastic deformation and failure modes are able to further illustrate the physical meaning of critical loads.

5:00pm **SE-TuA9 Corrosion Resistance of Mechanically Reinforced Aluminium based Coatings obtained by PVD Techniques***, **Frederic Sanchette**,* UTT - Université de Technologie de Troyes, France*; J. Creus,* Université de La Rochelle, France*; A. Billard,* FEMTO-ST, France **INVITED**

Aluminium-based alloy films can be used for the protection of steels against corrosion However, the mechanical properties of such coatings must be reinforced, for example by addition of transition elements, which have low diffusivity and low solubility in aluminum. Various aluminium based alloys elaborated by Electron Beam Physical Vapour Deposition (EBPVD) or magnetron sputtering techniques are characterised in terms of mechanical properties and corrosion behaviour in saline solution. The incorporation of transition metals permits to modify the mechanical or physico-chemical characteristics of aluminium coatings, so several alloying elements are compared. Evolution of microstructure of the Al based coatings is discussed versus the alloying element content. Different compositions of alloys are examined.

This presentation summarizes the main results of studies conducted in this field since the early 1990s. This is a synthesis of the main tendencies reported during the evaluation of the mechanical and corrosion properties of these alloys.

The objective is to build a reactivity classification in saline solution of several Al based coatings synthe- sized by vacuum deposition techniques. Combined with the classification of mechanical properties, these standards would become relevant guides in the choice of PVD coatings and/or alloys for applications exposed to saline environments. In our study, this guide is helpful in the synthesis of nanometric multi- layer architectures, which proves to be a promising way to combine improved mechanical properties with sacrificial character for the future coating configurations.

5:40pm **SE-TuA11 High Temperature Mechanical Properties of CrAlN and CrAlSiN Hard Coatings***, **Aljaž Drnovšek**, M. Rebelo de Figueiredo, A. Xia,* Montanuniversität Leoben, Austria*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; H. Vo, P. Hosemann,* Univeristy of California Berkeley*; R. Franz,* Montanuniversität Leoben, Austria

One of the most common methods used to characterize the mechanical properties of hard coating materials is nanoindentation. The further development of nanoindentation in recent years led to new ex-situ and in-situ systems that are capable of measuring mechanical properties such as hardness, elastic modulus and fracture toughness at elevated temperatures. In addition, new measuring procedures such as nano-dynamic mechanical analysis (n-DMA) enable measuring the hardness and elastic modulus at a continuous rate through the entire penetration depth at reduced thermal drift sensibility. This approach yields faster measurements at high temperatures which is beneficial in terms of tip degradation and generally renders the obtained results more reliable. With these new experimental possibilities, the mechanical properties of hard coatings synthesized by physical vapor deposition techniques can now be characterized close to the service temperatures that can reach up to 1000 °C.

In the current work, we tested two magnetron sputtered coatings that are widely used in industrial cutting applications, namely CrAlN and CrAlSiN. The latter is a further development of CrAlN coatings where the columnar growth is interrupted due to the addition of Si resulting in a nanocomposite composed of crystalline CrAl(Si)N grains and an amorphous SiN_x grain boundary phase. In particular in the case of CrAlSiN hard coatings, studies analyzing the mechanical properties at high temperature are scarce. High temperature nanoindentation measurements on both coatings were performed up to 700 °C in steps of 100 °C. The room temperature hardness values of 30 GPa (CrAlN) and 36 GPa (CrAlSiN) reduced by approximately 2 GPa per temperature step up to 500 °C. Above this temperature, the hardness of CrAlN continued to decrease while the hardness of CrAlSiN remained largely unchanged. In addition, high temperature tribological tests were conducted in air and inert atmosphere in the same temperature range in order to link the friction and wear behavior to the obtained mechanical properties. This data set is intended to serve as a first step towards a more comprehensive understanding of the high temperature mechanical and tribological properties of hard coatings which is vital for their further development and improvement.

6:00pm **SE-TuA12 Thick CrN/AlN Superlattice Coatings for Solid Particle Erosion and High Temperature Wear Resistant Applications***, **Jianliang Lin**,* Southwest Research Institute

Energetic ion bombardment is critical to improve the structure and properties of coatings in plasma assisted depositions. Plasma enhanced magnetron sputtering (PEMS) is an advanced version of conventional magnetron sputtering by generating a global plasma, in addition to the magnetron plasma, in the entire deposition system using hot filament thermionic emission to enhance the ionization and bombardment. In this study, thick CrN/AlN superlattice coatings (15 to 20 µm) were deposited by reactive sputtering using a combination of PEMS and high power impulse magnetron sputtering (HiPIMS) techniques. These coatings were deposited at different PEMS plasma discharge currents (0 to 4 A) which represent different ion fluxes for the bombardment. The bilayer thickness of the nanolayers was controlled in the range of 4 to 7 nm. The microstructure of the coatings gradually changes from long columnar grains to extremely dense structure with an increase in the PEMS discharge current. These coatings exhibited high hardness, excellent adhesion, and excellent resistance to high temperature wear, oxidation and solid particle erosion. The high temperature wear resistance of selected coatings was measured using a high temperature pin-on-disc tribometer in the ambient air from 600 °C to 1000 °C. The solid particle erosion resistance of these thick CrN/AlN coating was evaluated and compared with other thick hard coatings, e.g. CrN, TiN, TiSiCN, etc., using an air jet sand erosion tester. In this presentation, PEMS/HiPIMS deposition process, the coating microstructures, erosion, and high temperature wear test results will be discussed.

Surface Science Division
Room 203C - Session SS+HC+MI-TuA
Oxides/Chalcogenides: Structures and Reactions

Moderator: Andrew Teplyakov, University of Delaware

2:20pm **SS+HC+MI-TuA1 New Eyes for Nanocatalysis: Atomic Scale Investigations of TiO_2 Chemistry***, **Melissa Hines**,* Cornell University **INVITED**

The atomic-scale surface chemistry of nanocatalysis has remained relatively unexplored for two simple reasons. First, nanocatalysts are too small to be studied individually with most surface science techniques. Second, nanocatalysts are typically used at ambient pressure or in solution — conditions where surface contamination is a significant concern. In this talk, I will review our work in developing “new eyes for nanocatalysts” that address both issues.

Addressing the issue of size, I will show that hydrothermal crystal growth techniques can produce anatase nanocrystals suitable for study at the atomic-scale with STM and a panoply of techniques. Despite being synthesized in solution, the nanocrystal surfaces are very clean and passivated by a protecting monolayer. Using these crystals, I will show that the most commonly used functionalization chemistry for oxide nanocatalysts, a carboxylic acid solution, causes the spontaneous reorganization of the nanocatalyst, leading to *a five-fold increase in the number of reactive sites.*

Addressing the issue of contamination, I will explain the chemical origin of the molecularly ordered interfaces that have been observed by researchers around the world when TiO_2 surfaces are exposed to air or solution. Although these structures have recently been attributed to a new (2 × 1) ordered state of adsorbed H_2O, we show that clean TiO_2 surfaces selectively adsorbs atmospheric organic acids that are typically present in parts-per-billion concentrations while effectively repelling other adsorbates, such as alcohols, present in much higher concentrations. This finding may have important implications for TiO_2 photocatalysis, as the self-assembled carboxylate monolayer resists desorption under environmental conditions while effectively blocking the transition metal sites typically implicated in photocatalysis.

As time allows, I will also show that solution-phase techniques can be used to prepare a wide variety near-atomically-perfect, self-assembled monolayers on TiO_2 surfaces.

3:00pm **SS+HC+MI-TuA3 Coverage-dependent Water Agglomerates on Fe_3O_4 Surfaces**, ***Zdenek Jakub***, Vienna University of Technology, Austria; *M. Meier,* University of Vienna, Austria; *J. Hulva, J. Pavelec, M. Setvin, M. Schmid, U. Diebold,* Vienna University of Technology, Austria; *C. Franchini,* University of Vienna, Austria; *G.S. Parkinson,* Vienna University of Technology, Austria

The interaction between iron oxides and water plays a key role in many natural and technological processes. Recent water adsorption studies have found significant complexity on metal oxides, with reports of mixed-mode adsorption and hydrogen bonding. Here we present a multi-technique study of water adsorption on Fe_3O_4 surfaces. Utilizing quantitative temperature programed desorption (TPD) and X-ray Photoelectron Spectroscopy (XPS), we identify four partially dissociated phases in the submonolayer regime on the $Fe_3O_4(001)$, corresponding to coverages of 9, 8, 6 and 3 molecules per surface unit cell. These are investigated by non-contact atomic force microscopy (nc-AFM) with tip functionalized by CO molecule, and the observed structures are further interpreted by DFT-based calculations. We clearly demonstrate the existence of partially dissociated dimers and trimers at lower coverage, and a build-up of complex hydrogen-bonded network with increasing coverage. Applying the same approach on the $Fe_3O_4(111)$ we discuss the general trends of water adsorption on Fe_3O_4 surfaces.

3:20pm **SS+HC+MI-TuA4 Reversible Structural Evolution and Identification of the Catalytically Active Phase of $NiCoO_xH_y$ During the Oxygen Evolution Reaction (OER)**, ***Bruce E. Koel***, Princeton University

Significant improvements in the activity of transition metal oxides (TMOs) for the oxygen evolution reaction (OER) have been made by tailoring the morphology and crystal structure of the catalysts, incorporating dopants, and using conductive supports. However, the complex composition and structure of TMO catalysts have hindered the elucidation of clear structure-activity correlations. We have utilized a range of electrochemical techniques, such as electrical impedence spectroscopy (EIS), and spectroscopic techniques, including ambient pressure photoelectron spectroscopy (APPES), for characterization of pure and Ni-modified cobalt (oxy)hydroxide electrocatalysts for OER. In particular, operando Raman spectroscopy and electrochemical techniques were used during the oxygen evolution reaction to identify the composition and local structure of electrodeposited CoO_xH_y and $NiCoO_xH_y$ catalyst films. In these studies, several unique initial catalyst structures and crystallinities were prepared by subjecting the samples to a variety of thermal and electrochemical conditioning procedures before evaluation. During oxygen evolution, Ni-modified CoO_xH_y films with lower initial crystallinity underwent substantial structural evolution that began with an irreversible transformation of a spinel local structure to an amorphous CoO structure at low anodic potentials. Increasing anodic polarization with elevated oxygen evolution rates caused additional structural conversion of the amorphous CoO structure to a complex phase that can be described as an amalgamation of NiOOH and layered CoO_2 motifs (NiOOH-h-CoO_2). The formation of this active structure was correlated with improved OER activity. Formation during oxygen evolution of the same NiOOH-h-CoO_2 structure independent of the initial cobalt oxide structure suggests that this active phase identified in these studies could be the universally active structure for $NiCoO_xH_y$ catalysts.

4:20pm **SS+HC+MI-TuA7 Understanding the Growth and Chemical Activity of Titania-Supported MoS_x Clusters**, ***Donna Chen,*** University of South Carolina; *R.P. Galhenage,* University of California at Irvine; *H. Yan,* University of Louisiana Layfette; *D. Le, T.B. Rawal, T.S. Rahman,* University of Central Florida

MoS_x clusters have been grown on $TiO_2(110)$ in order to provide a model surface for better understanding adsorbate interactions and chemical activity of supported MoS_x clusters; MoS_2 particles have exhibited excellent catalytic activity for a variety of reactions, particularly for hydrodesulfurization and photocatalysis, and interactions with the support are believed to induce new electronic properties. The MoS_x clusters were grown by deposition of Mo on titania in an atmosphere of H_2S, followed by annealing to 950 K in H_2S. Scanning tunneling microscopy experiments show that clusters with elongated, rectangular shapes and flat tops are formed, and the long axes of the clusters have specific orientations with respect to the [001] direction on $TiO_2(110)$. In contrast, deposition of Mo in the absence of H_2S results in a high density of smaller, round clusters that cover the majority of the surface. The morphologies of MoS_x clusters do not change after exposure to various gases (D_2, CO, O_2, methanol) in ultrahigh vacuum. However, exposure to higher pressures of O_2 (250 mTorr) or air causes the clusters to disintegrate as Mo in the clusters becomes oxidized. Temperature programmed desorption studies with CO on the MoS_x clusters show a distinct desorption peak at 275 K, which is not observed on metallic Mo or titania. Density functional theory calculations demonstrate that the presence of the titania support changes in the favored adsorption site for CO from the (-1010) edge in the pristine MoS_2 to the (10-10) edge for the supported MoS_2. Furthermore, the $MoS_x/TiO_2(110)$ interfacial sites are not favored for CO adsorption.

*This work is partially supported by DOE grant DE-FG02-07ER15842.

4:40pm **SS+HC+MI-TuA8 Analyzing Single Atom Catalysts using Low Energy Ion Scattering (LEIS)**, ***Thomas Grehl***, IONTOF GmbH, Germany; *R. ter Veen,* Tascon GmbH, Germany; *D. Kunwar, A. Datye,* University of New Mexico; *H.H. Brongersma,* IONTOF GmbH and Tascon GmbH, Germany

An important goal of heterogeneous catalyst synthesis is the dispersion of the active metal uniformly on a catalyst support, ideally achieving atomic dispersion. Isolated atoms dispersed on oxide supports (single-atom catalysts) provide efficient utilization of scarce platinum group metals, and higher reactivity as well as better selectivity for a range of catalytic reactions.

One of the challenges is to achieve high enough loadings and to prevent agglomeration by limiting the synthesis and operation temperature. Consequently, the characterization of these materials is essential to monitor the dispersion.

Low Energy Ion Scattering (LEIS) is a surface analytical technique that quantitatively determines the elemental composition of the outer atoms with ultimate surface sensitivity. LEIS is compatible with non-conducting supports and insensitive to topography, making it an ideal tool to analyze both model and industrial catalysts. Due to its unique surface sensitivity the results of the analysis usually correlate directly with the properties of the catalyst.

This contribution demonstrates the analysis of Pt/CeO_2 single atom catalysts using LEIS. During synthesis (atom trapping) the Pt precursor is heated in air at 800 C to form mobile Pt species that deposit on the support and are strongly bound. On high surface area ceria, metal loadings of 3 wt. % can be achieved while maintaining almost exclusively single atoms. We will describe how LEIS was essential to demonstrating the single atom nature of the catalyst. In conjunction with X-ray absorption spectroscopy (XAS), Aberration-Corrected Scanning TEM (AC-STEM) and Diffuse Reflectance Infrared Absorption Spectroscopy (DRIFTS) we were able to develop an accurate picture of the sites that bind Pt ions on the support. The atomistic model for the single atom Pt catalyst was corroborated by Density Functional Theory (DFT).

The LEIS results revealed that with increasing metal loading, the fraction of Pt visible to LEIS decreased by 20%. However XAS, DRIFTS and AC-STEM confirmed that the Pt was present in single atom form even at the highest metal loadings. Further analysis led to the realization that the Pt atoms are present in close proximity at high loadings, causing some of the Pt to be rendered invisible to LEIS. The loss in LEIS signal could be correlated with the differences in reactivity for CO oxidation, which otherwise could not be easily explained. This application demonstrates the extreme sensitivity of LEIS which makes this analytical approach essential for study of heterogeneous catalysts used in industry.

Part of this work was supported by DOE grant DE-FG02-05ER15712 and NSF grant EEC-1647722.

5:00pm **SS+HC+MI-TuA9 Synthesis and Characterization of Metals Supported on ZnO Nanoparticles**, ***Amanda Haines***, *D.F. Ferrah, J.C. Hemminger,* University of California at Irvine

Various metals on transition metal oxide supports, such as Cu/ZnO, have been widely studied to understand their role in CO_2 hydrogenation. However, there still remains a dispute as to the role of the oxide supports and the surface oxidation state of the active metal and its efficacy in the reduction of CO_2, namely on the nature of CO_2 adsorption and activation. Here, we have designed and characterized a model catalytic system that will enable us to explore the chemistry of various metals (M_i: i=Pt,Cu) on ZnO supports. ZnO nanoparticles (NPs) have been deposited on an inert highly oriented pyrolytic graphite (HOPG) substrate by physical vapor deposition (PVD). From scanning electron microscopy (SEM), we have seen that hexagonal shaped ZnO nanoparticles are formed on a defect-free HOPG substrate. Different surface plasma treatments have been explored to create defect sites on the HOPG substrate to better control the density of the ZnO NPs and various substrate temperatures have been studied to investigate its effect on the size, morphology, structure and chemistry of the NP growth process. Different metals, Pt and Cu, are photodeposited on the ZnO NPs and fully characterized using X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and temperature programmed desorption (TPD) to gain fundamental information about the oxidation states and active sites of these M_i/ZnO NPs. Future work will involve reactivity studies on the fully characterized M_i/ZnO NPs using ambient pressure X-Ray photoelectron spectroscopy (AP-XPS) to investigate the surface chemistry, intermediates and products of this catalyst to gain insight into the reaction mechanism of CO_2 hydrogenation.

5:20pm **SS+HC+MI-TuA10 Molecular Water Adsorption and Reactions on α-Al_2O_3(0001) and α-Alumina Particles**, ***Greg Kimmel***, *N.G. Petrik,* Pacific Northwest National Laboratory; *P.L. Huestis, J.A. LaVerne,* University of Notre Dame; *A.B. Aleksandrov, T.M. Orlando,* Georgia Institute of Technology

Alumina and its interactions with water are important in areas ranging from electronics and catalysis to environmental science. However, a basic understanding of the adsorption and reactions of water on even the simplest alumina surface, the (0001) surface of α-alumina, remains elusive. We have investigated the adsorption and reaction of water on single crystal, α-Al_2O_3(0001) in ultrahigh vacuum, and α-alumina particles in ambient conditions, using temperature programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), and other surface science techniques. For a water coverages of 1 and 2 H_2O/(surface Al^{3+}) on α-Al-$_2O_3$(0001), no evidence for the surface hydroxyls expected from dissociative adsorption was observed, while the ν_2 vibration of molecular water was observed. Electron-stimulated desorption of molecular water at low coverages also indicated molecular or mixed (molecular plus dissociative) adsorption. In contrast with the single crystal results, IR spectra of water adsorption on alumina particles indicated the presence of surface hydroxyls that persist even after annealing to high temperatures in oxygen. The results, which are consistent with at most a small amount of water dissociation on the Al-terminated (0001) surface, are difficult to reconcile with calculations suggesting that the barrier to dissociation is small. However, the results are consistent with recent vibrational sum frequency experiments showing that the hydroxylation of the Al-terminated (0001) surface takes many days even at ambient pressures and temperatures.

5:40pm **SS+HC+MI-TuA11 Applying Low Temperature Titration for Determination of Metallic Sites on Active Oxide Supported Catalysts**, ***Jerry Pui Ho Li***, *Z. Liu, Y. Yang,* ShanghaiTech University, China

Catalysts are used in a variety of applications from the production of fuels or consumer chemicals, and the environment. Characterization of such catalysts is critical, since it allows for an accurate representation of its effectiveness. For optimum design and efficient utilization of catalysts, it is important to be able to connect model catalyst and industrial catalyst turnover frequencies (TOF) based on the same benchmark for active sites, such as metallic sites, for catalyst evaluation and further kinetics studies. Characterization of the active sites with chemisorption is ideally performed with high time resolution and sensitivity; particularly for catalysts with low loading of the active particles.

Chemisorption study is the common method for active site determination, but has limitations for active heterogeneous catalysts; particularly industrial catalysts because the method often cannot distinguish the redox on metallic sites and catalyst support. An online micro reactor combined with online mass spectroscopy was developed for kinetics studies within wide temperature (as low as liquid nitrogen) and pressure ranges. Pt and Cu based catalysts are used as demonstration of this technique for metallic sites quantitative calibration in this study. Pt catalysts were characterized using CO oxidation and Cu catalysts were characterized using N_2O decomposition. By comparing titration products curves (CO_2 for Pt catalysts, and N_2 for Cu catalysts) versus temperature for both supported samples, narrow subzero temperature windows are found for each catalyst, demonstrating that the titration products are only related with metallic sites. Pure metallic powder was analyzed for confirmation. Specialized chemisorption procedure was established for each sample. This procedure shows a reliable direct titration measurement recipe for the characterization of supported catalysts, quantifying only the metallic sites for catalysts while being selective against surfaces that contribute secondary reactions often found with more complex supports.

We also present a specialized chemisorption technique applied for metallic sites determination of Au nanoparticles on TiO_2 support through CO at low temperature by comparing IR assignment.

6:00pm **SS+HC+MI-TuA12 Giant Optical Anisotropy in Hexagonal Perovskite Chalcogenides with Quasi-1D Structures**, ***Shanyuan Niu***, University of Southern California; *G. Joe,* University of Wisconsin - Madison; *H. Zhao, M. Mecklenburg,* University of Southern California; *T. Tiwald,* J.A. Woollam Co. Inc; *K. Mahalingam,* Air Force Research Laboratory; *H. Wang,* University of Southern California; *M. Kats,* University of Wisconsin - Madison; *J. Ravichandran,* University of Southern California

Optical anisotropyis a crucial building block to engineer the polarization of light in polarizing optics, light modulators, imaging and communication systems. While metamaterial architectures with form birefringence can overcome the limited optical anisotropy available in widely used natural anisotropic crystals, their deployment is limited by the demanding fabrication. We demonstrate the realization of giant optical anisotropy via chemically engineering the polarizability tensor in a natural material, $BaTiS_3$, which has a highly anisotropic quasi-1D structure and features easily accessible in-plane anisotropy. Large single crystals were grown with the chemical vapor transport method. We report the observation of a large, broadband infrared birefringence and linear dichroism. As-grown crystals demonstrate strong dichroism with two distinct optical absorption edges for light with polarizations along two principal axes. To our knowledge, the unprecedented birefringence in the transparent region is more than twice as large as that in any other bulk crystal.

Thin Films Division
Room 104B - Session TF+PS-TuA

Atomic Layer Processing: Chemistry & Surface Reactions for Atomic Layer Processing

Moderators: Jessica Kachian, Intel Corporation, Keren Kanarik, Lam Research Corporation

2:20pm **TF+PS-TuA1 N-heterocyclic Carbenes on Au and Cu Surfaces**, ***Cathleen Crudden***, Queen's University, Canada **INVITED**

N-Heterocyclic carbenes (NHCs) are an exciting new class of ligand for metal surfaces, with potentially interesting applications in patterning and surface functionalization. In this talk, we will address the use of NHCs as ligands for various metal surfaces including coinage and other metals. The functionalization of flat and structured surfaces will be presented and potential applications in etching.

3:00pm **TF+PS-TuA3 Enhancing Nucleation in Platinum Atomic Layer Deposition by Surface Pre-Treatment with Small Organometallic Molecules**, ***Camila de Paula***, *L. Zeng, S.F. Bent,* Stanford University

Pt thin films have a wide variety of applications in microelectronics, catalysis, and energy technologies. Since most of these applications require a conformal and pinhole-free thin film, achieving good nucleation is an important requirement. It is believed that a low abundance of dissociated oxygen atoms in the initial stages of the Pt ALD process leads to a nucleation delay and island growth. The nucleation and growth mechanisms have a big impact on the properties of the resulting thin film. If nucleation is inhibited, isolated particles rather than a continuous film may be deposited at low cycle numbers (island-growth), whereas if nucleation is facile, a continuous film may be formed at much lower thicknesses.

While there have been studies focused on the surface reactions that occur during Pt ALD, there is still a lack of understanding of how the substrate surface properties affect nucleation in the initial stages of ALD. There have been reports of methods aimed at enhancing nucleation for specific substrates, such as using a wet piranha etch on silicon substrates. Other studies have used high surface energy adhesion layers, such as W, in order to overcome the nucleation delay.

The goal of this study is to develop a surface pre-treatment technique that enhances Pt ALD nucleation independent of substrate choice, while inducing minimum surface modification of the substrate. In this work, the influence of a sub-monolayer surface coverage of small organometallic molecules on the nucleation and growth of Pt by ALD was studied. It was observed that introducing a short pulse of dimethylaluminum chloride (DMACl) prior to Pt deposition leads to the formation of a continuous film after fewer than 100 cycles on thermally grown silicon oxide vs. over 200 cycles on a non-treated sample. Scanning electron microscopy (SEM), synchrotron based grazing incidence small angle X-ray scattering (GISAXS) and X-ray photoelectron spectroscopy (XPS) were used to analyze the ALD growth mechanism on various treated and untreated substrates. The formation of densely-packed large Pt nanoparticles was observed on the treated surface. GISAXS analysis of the Yoneda-Peak position and pattern showed that the surface treatment leads to nanoparticle coalescence in the very early stages of ALD. Interestingly, a comparison of DMACl to other small organometallic molecules showed that some molecules induced the opposite behavior, instead leading to inhibited Pt ALD. The detailed growth mechanism and possible reaction pathways leading to these results will be discussed.

3:20pm **TF+PS-TuA4 Mass Spectrometer Studies of Volatile Etch Products Produced by Ligand-Exchange Reactions During Thermal Atomic Layer Etching**, ***Joel Clancey**, A.S. Cavanagh, S.M. George,* University of Colorado Boulder

Atomic layer etching (ALE) using sequential, self-limiting surface reactions is an important technique for removing material with atomic layer control. In addition, selective ALE is required for the maskless fabrication of advanced devices as feature sizes become smaller than available lithography. This study reports the study of volatile etch products produced by ligand-exchange reactions during thermal ALE and develops our understanding of selective thermal ALE.

Previous studies have revealed selective thermal ALE in the etching of Al_2O_3, ZrO_2 and HfO_2 using fluorination and ligand-exchange reactions [1]. In this work, we used metal fluoride powders to study volatile etch products produced by fluorination and ligand-exchange reactions during thermal ALE. An *in situ* quadrupole mass spectrometer (QMS) was employed to characterize the etch products produced during the thermal etching of AlF_3, ZrF_4 and HfF_4 powders between 200°C and 300°C using TMA, DMAC, $SiCl_4$ and $TiCl_4$ as the metal precursors.

Thermal Al_2O_3 ALE occurs using HF and TMA as the precursors [2]. For the reaction of TMA with AlF_3 powders, the observed etch products are dimers such as $[AlF(CH_3)_2]_2$ and $[AlF(CH_3)_2\text{-}Al(CH_3)_3]_2$. These products are equivalent to the dimer etch products observed earlier for the reaction of TMA with fluorinated Al_2O_3 during thermal Al_2O_3 ALE. In contrast, Al_2O_3 ALE does not occur with either $SiCl_4$ or $TiCl_4$ as the metal precursors [1]. For the reaction of $SiCl_4$ and $TiCl_4$ with AlF_3 powders, the observed reaction products are $SiFCl_3$ and $TiFCl_3$, respectively. There is halide-exchange between the $SiCl_4$ and $TiCl_4$ metal precursors and the AlF_3 surface. However, there is no observation of volatile Al-containing products that would be consistent with Al_2O_3 etching.

We are developing a matrix that correlates volatile etch or ligand-exchange products with the previous etching results. We are also using density functional theory (DFT) to predict the etch products during thermal ALE. These DFT calculations correctly predict the dimer etch products during Al_2O_3 ALE. This approach is advancing our understanding of selective thermal ALE.

[1] Younghee Lee, Craig Huffman, and Steven M. George, "Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions", *Chem Mater*. **28**, 7657 (2016).

[2] Younghee Lee, Jaime W. DuMont and Steven M. George, "Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions", *Chem. Mater.* **28**, 2994 (2016).

5:00pm **TF+PS-TuA9 Calculations of Etch Products from Thermal Atomic Layer Etching Using Fluorination and Ligand-Exchange Reactions**, ***Andrew Cavanagh**, J.W. Clancey, S. Sharma, S.M. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of Al_2O_3 can be accomplished using sequential, self-limiting fluorination and ligand-exchange surface reactions with hydrofluoric acid (HF) and trimethyl aluminum (TMA, $Al(CH_3)_3$) as the precursors. Fluorination by HF converts the surface of Al_2O_3 to AlF_3. Ligand-exchange reactions then occur between TMA and the AlF_3 surface. The first ligand-exchange reaction is believed to be: $AlF_3(s) + Al(CH_3)_3(g) \rightarrow AlCH_3F_2(s) + Al(CH_3)_2F(g)$ where "s" indicates a surface species and "g" indicates a gas phase species. Additional ligand-exchange reactions can then react $AlF_2CH_3(s)$ to $AlF(CH_3)_2(g)$. Recent quadrupole mass spectrometry (QMS) studies have observed that the main etch products during Al_2O_3 ALE are the dimers $AlF(CH_3)_2\text{-}AlF(CH_3)_2$ and $AlF(CH_3)_2\text{-}Al(CH_3)_3$. These dimers may be formed from the monomer $AlF(CH_3)_2$ etch product pairing with itself or with the $Al(CH_3)_3$ metal precursor.

To understand these dimer etch products, density functional theory (DFT) calculations were performed on all possible dimers that could be produced from the four possible monomer species ($Al(CH_3)_3$, $Al(CH_3)_2F$, $AlCH_3F$, AlF_3). Each dimer consisted of a pair of bridging ligands between the two Al metal centers and four terminal ligands. The bridging ligands could be (F, F), (F, CH_3) or (CH_3, CH_3). The (F, F) bridges resulted in the most stable dimers while the (CH_3, CH_3) bridges resulted in the least stable dimers. In agreement with the QMS results, these DFT calculations predict that the $AlF(CH_3)_2\text{-}AlF(CH_3)_2$ dimer with a (F,F) bridge and four terminal methyl groups is the most viable etch product.

Additional DFT computational studies have also been performed for ligand-exchange reactions on fluorinated surfaces of Al_2O_3, ZrO_2 and Ga_2O_3 with various metal precursors including $Al(CH_3)_3$, $Al(CH_3)_2Cl$, $SiCl_4$, $GeCl_4$, $SnCl_4$, and $TiCl_4$. These calculations model the ligand-exchange surface reactions during Al_2O_3, ZrO_2 and Ga_2O_3 ALE. For all systems studied to date, the calculations indicate that dimer species are the preferred etch products. Future QMS experiments will observe etch products and compare with the DFT computational studies for a more complete understanding of thermal ALE.

5:20pm **TF+PS-TuA10 Formation of Monolayers and Multilayers During the Vapor-Phase Deposition of Dodecanethiols on Copper Oxide**, ***David Bergsman**, T-L. Liu, R.G. Closser, S.F. Bent,* Stanford University

The deposition of alkanethiols onto copper and copper oxide has been widely studied for use in the passivation of surfaces and as ultrathin blocking layers. The formation of alkanethiol self-assembled monolayers (SAMs) on copper oxide is particularly interesting in that thiols are known to etch and reduce copper oxide surfaces before ultimately forming a SAM. This has sometimes resulted in films much thicker than expected for a monolayer, leading to the hypothesis that this etching process can create multilayers, though the structure of those multilayers and the mechanism behind their formation were not explored. In recent years, the use of SAMs to enable area-selective atomic layer deposition (ALD) for back-end semiconductor processing has created renewed interest in the study of thiol deposition onto copper, particularly through vapor-phase approaches that can be more easily incorporated into industrial semiconductor fabrication processes. However, no studies have reported the formation of Cu-thiolate multilayers through the vapor-phase.

In this work, we examine the vapor deposition of dodecanethiols (DDTs) onto copper and copper oxide surfaces. We show using atomic force microscopy, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy/electron energy loss spectroscopy that this deposition onto copper oxide surfaces results in the formation of up to 8 nm thick Cu-thiolate multilayer films, rather than SAMs. In contrast, pre-removal of the copper oxide and subsequent DDT exposure creates 2 nm thick SAMs, suggesting that the etching of the copper oxide films by thiol molecules is a key step in the multilayer formation. Synchrotron-based grazing-incidence X-ray diffraction shows these thick films to be highly crystalline, with bilayer thiol structures sandwiched between layers of copper atoms. Crystallites are shown to be oriented both perpendicular and parallel to the surface. We further explore the degradation of these multilayers, demonstrating with scanning electron microscopy and XPS that the films appear to dewet into micron-sized particles after exposure to air. Continued air exposure results in the oxidation of the sulfur and copper in the films on a time scale consistent with DDT monolayers. Finally, the implications of this multilayer formation on area-selective ALD will be discussed.

5:40pm **TF+PS-TuA11 Exchange Reactions During Atomic Layer Deposition: ZnO Conversion to Al_2O_3 by Trimethylaluminum**, ***Tyler Myers**, A.M. Cano, J.W. Clancey, D.K. Lancaster, S.M. George,* University of Colorado at Boulder

Atomic layer deposition (ALD) is typically described by the self-limiting reaction of precursors with surface species that leads to controlled thin film growth. Missing from this picture is the possibility that the precursors can also undergo exchange reactions and convert the surface of the initial substrate to a new material. These exchange reactions are expected if the conversion produces a more thermodynamically favorable reaction product. These exchange reactions may be common during ALD nucleation.

In this study, the exchange between Zn and Al is explored during the initial reaction of trimethylaluminum (TMA) on ZnO films during Al_2O_3 ALD at temperatures from 150-250°C. The exchange is evident from a variety of experimental measurements. Fourier transform infrared (FTIR) investigations detect absorbance changes consistent with ZnO loss and Al_2O_3 gain after the TMA reaction on ZnO ALD films. Quadrupole mass spectrometry (QMS) measurements also observe $Zn(CH_3)_2$ reaction products as expected from the conversion reaction: $3ZnO + 2Al(CH_3)_3 \rightarrow Al_2O_3 + 3Zn(CH_3)_2$. In addition, studies of the effect of TMA exposures on ZnO nanoparticles with a diameter of ~10 nm measured the conversion of ZnO to Al_2O_3. The conversion produces a large mass loss that is consistent with the formation of an Al_2O_3 surface layer. The ZnO to Al_2O_3 conversion is also self-limiting as a function of TMA exposure.

X-ray photoelectron spectroscopy (XPS) and X-ray reflectivity (XRR) investigations are also consistent with the conversion of the surface of ZnO ALD films to Al_2O_3 after the initial TMA exposure. The XPS and XRR measurements both yield an Al_2O_3 surface layer with a thickness of ~1.0 nm on the ZnO ALD film. In addition, quartz crystal microbalance (QCM) measurements detect a substantial conversion of ZnO to Al_2O_3 after the initial TMA exposure during Al_2O_3 ALD. The QCM studies reveal that the mass losses are much more pronounced for thin ZnO films compared with thick ZnO films. In addition, the mass losses are more for ZnO surfaces terminated with $Zn-CH_3CH_3$ species compared with Zn-OH species.

These studies of the exchange between Zn and Al during the initial reaction of TMA on ZnO illustrate that ALD precursors can convert the surface of the initial substrate to a new material. These exchange reactions must be considered when analyzing ALD nucleation.

6:00pm **TF+PS-TuA12 3D Feature Profile Simulation Coupled with Realistic Plasma Surface Reaction Model for ALE Process*, YeongGeun Yook*,** *H.S. You, J.H. Park,* Chonbuk National University, Republic of Korea*; D.H. You,* KW Tech, Republic of Korea*; K.S. Choi,* Chonbuk National University, Republic of Korea*; W.S. Chang,* National Fusion Research Institute, Republic of Korea

Recently, atomic layer etching (ALE) processes have attracted much interest for sub-10nm semiconductor fabrication process. Notably, a cyclic plasma-enhanced fluorocarbon ALE process using the conventional plasma etch tools has investigated for its selective etching and atomic-level control. In spite of its superior merits, the detailed studies remain to apply sub-10nm 3D nanoscale feature patterns due to its complexity. To address this issue, we developed a 3D feature profile simulator which was composed of a Zero-D bulk plasma simulator, a multiple-level set moving algorithm based on a hash map, a GPU based ballistic transport algorithm, and a surface reaction model. In this work, we focus on the development of a transient surface reaction model of ALE process to capture the realistic surface reaction. Finally, 3D feature profile simulations coupled with the surface reaction model were verified with experimental data. We believe that this approach enables us to understand unveiled phenomena of ALE process.

Thin Films Division
Room 102A - Session TF+SS-TuA
Organic/Inorganic Materials and Interfaces

Moderator: Matthew Richard Linford, Brigham Young University

2:20pm **TF+SS-TuA1 Chemical Interactions at Hybrid Interfaces: An In Situ Investigation of Organic/Inorganic Systems*, Sven Pletincx,*** Vrije Universiteit Brussel, Belgium*; L. Trotochaud,* Lawrence Berkeley Lab, University of California, Berkeley*; L.-L. Fockaert, M. Meeusen, J.M.C. Mol,* Technical University Delft, Netherlands*; H. Bluhm,* Lawrence Berkeley Lab, University of California, Berkeley*; H. Terryn, T. Hauffman,* Vrije Universiteit Brussel, Belgium

The durability of hybrid systems is mainly determined by the different phenomena occurring at the organic/inorganic interface. However, analyzing this solid/solid or liquid/solid interface under technologically relevant conditions is challenging. Recently, the *in situ* investigation of these so-called buried interfaces is done by monitoring ultrathin polymer films onto a metal oxide substrate by ambient-pressure photoelectron spectroscopy (APXPS).[1,2] Here, we show that APXPS with a conventional X-ray source can be used to study the effects of water exposure on the interaction of different acrylic coatings with aluminum oxide.

The deposition of this nanometer thin overlayer is often carried out by reactive adsorption from dilute polymer solutions. However, the influence of the solvent on the metal oxide chemistry is seldom taken into account in interface studies. An integrated spectroelectrochemical setup of ATR-FTIR Kretschmann and Odd Random Phase multisine Electrochemical Impedance Spectroscopy (ORP-EIS) allows to monitor the influence of the solvent on the metal oxide surface. An aluminum layer is sputtered on an IR transparent crystal, the IR signal at the interface is amplified because of the Kretschmann effect, and a near-interface spectrum of the organic/oxide surface is obtained. The occurring interface processes can be followed with infrared spectroscopy while simultaneously, the PVD layer acts as a working electrode. This allows to determine the electrochemical properties of the overall hybrid system, studied by ORP-EIS.[3]

After the characterization of the solvent interactions, *in situ* ATR-FTIR Kretschmann/ORP-EIS is used to study the effect of an electrolyte on an acrylic polymer/metal oxide system. This way, we have direct access to the interface, and the influence of an above-the-polymer electrolyte (i.e. H_2O) can be probed. Also the study of covalent bonding, such as the interfacial interactions of silane adhesion promotors are investigated. This work shows that by using ultrathin films and a set of recently developed techniques, it is possible to non-destructively and *in situ* probe interfacial changes in hybrid systems.

1. Pletincx, S. *et al.* In Situ Characterization of the Initial Effect of Water on Molecular Interactions at the Interface of Organic/Inorganic Hybrid Systems. *Sci. Rep.***7,** 45123 (2017).

2. Pletincx, S. *et al.* Unravelling the Chemical Influence of Water on the PMMA/Aluminum Oxide Hybrid Interface In Situ. *Sci. Rep.***7,** 13341 (2017).

3. Hauffman, T. *et al.* Measuring the adsorption of ethanol on aluminium oxides using odd random phase multisine electrochemical impedance spectroscopy. *Electrochem. commun.***22,** 124–127 (2012).

2:40pm **TF+SS-TuA2 Microscopic and Spectroscopic evidence of Odd-Even Effect in Self-Assembled Monolayers of Biphenyl-Substituted Fatty Acid on Ag(111)*, Anna Krzykawska*,** Jagiellonian University, Polska*; P. Cyganik, M. Szwed, J. Ossowski,* Jagiellonian University, Poland

Self-assembled monolayers (SAMs) have been broadly studied as a model system for inorganic-organic interface in molecular electronics and biosensing devices. Current standard in SAMs formation is based on using sulfur as an anchoring group to the metal substrate. In our recent paper[1] we have indicated that by replacing thiol headgroup by carboxylic, a highly interesting alternative is obtained, particularly when 2D ordering, SAM fabrication time and stability in ambient conditions are of great importance. Following this first observation made for a specific system, in the current work we have investigated a homolog series of SAMs based on biphenyl-substituted fatty acids on Ag(111) in the form of $(C_6H_4)_2$-$(CH_2)_n$-COO/Ag (BP*n*COO/Ag, *n* = 1-4). The series of experiments were carried out using infrared reflection absorption spectroscopy (IRRAS), scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The results of this combined microscopic and spectroscopic analysis demonstrate very strong dependence of the structural properties on the number of the CH_2 groups in the short aliphatic linker. Monolayers with *n* = even show highly ordered and stable structures. In contrast, SAMs with *n* = *odd* have disordered liquid-like structure with more canted orientation of the molecular backbone and the carboxylic headgroup, which results in lower packing density and film thickness compared to the even-numbered SAMs. By comparing obtained results with former odd-even effects reported for analogues SAMs based on thiols and selenols[3,4], a common, qualitative model relating the odd-even effect to the monolayer stability and structure will be discussed. Our results demonstrate that for BP*n*COO/Ag, this odd-even effect is particularly strong and fully controls the ability of molecules to form highly ordered structures. This observation seems to be of key importance for the design of SAMs based on the carboxylic group, which, for correctly designed molecules, forms much better 2D-ordered structures compared to commonly used thiols.

References

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3:00pm **TF+SS-TuA3 CVD of Thin Polymer Films for Engineered Material Properties*, AnnaMaria Coclite,*** Graz University of Technology, Austria **INVITED**

Functional thin films offer innovative solutions for many technological applications: organic electronics, smart devices for biotechnology, microfluidics, membrane technology, sensors and drug delivery systems. The development of functional thin films, engineered to achieve all the desired properties, requires advanced growth techniques. The development of dry growth methods - based on vacuum- aims to complement and enlarge the applicability of functional thin films to fields where the presence of solvent is detrimental.

Successful results in terms of rationally designed micro- and nanoengineered materials will be demonstrated using as a case of study the growth of functional polymers by initiated CVD (iCVD). The high versatility of iCVD in driving application-specific properties into the material, creating a platform for the implementation of polymeric coatings into device fabrication will be discussed.

Layered nanostructures in proton conductive iCVD polymers were investigated though X-ray based methods. The polymers crystallize in a bilayer structure, perpendicular to the substrate surface, formed by perfluorinated pendant chains. Acid moieties were introduced to form ionic channels among the bilayers –parallel to the substrate surface- which can be responsible for proton conduction. This one-step polymerization process has the potential to manufacture inexpensive, high quality membranes for proton exchange membrane fuel cells.

Another case of study will be presented in the field of multi-stimuli-responsive materials. In particular, the material of interest in this case is a hydrogel that changes its size and shape when stimulated by light and humidity. Hydrogels are known for their dynamic swelling response to aqueous environments. A chemical functionalization of the hydrogel surface was performed to add other stimuli-responsive functionalities and obtain a smart material that responds to two stimuli. Modifying the hydrogel surface with solution-based methods is often problematic because of the damages caused by the permeation of solvents in the hydrogel. This issue is completely bypassed by the use of solvent-free techniques, like iCVD.

4:20pm **TF+SS-TuA7 Organosilicon Functionally Nanostructured Films as Engineered Interlayers for Hybrid Materials***, **Vladimir Cech**,* Brno University of Technology, Czech Republic*; J. Houdkova,* Institute of Physics, Academy of Sciences of the Czech Republic*; M. Branecky, T. Plichta,* Brno University of Technology*; J. Zemek,* Institute of Physics, Academy of Sciences of the Czech Republic

Thin films of organosilicones synthetized in low-temperature plasma constitute a class of materials with a rich and varied scientific background. This class of materials in the form of hydrogenated amorphous carbon-silicon (a-CSi:H) films has a distinctive characteristic that distinguishes it from other thin films – the ability to vary and control the degree of organic/inorganic character and crosslinking of carbon-silicon network by appropriate choice of fabrication variables. Oxygen atoms can be incorporated in organosilicon film to form new chemical bonds (Si-O, C-O, C=O) and vary the mechanical properties of hydrogenated amorphous carbon-silicon oxide (a-CSiO:H) films by modifying the carbon-silicon network. However, a multilayer rather than single layer film can fulfill specific functions not only in sophisticated electronic, optical, mechanical, and biomedical devices, but also in hybrid materials (composites and nanocomposites) with controlled interphase.

Functional multilayer nanostructures with controlled distribution of mechanical properties across the nanostructure were constructed from oxygen-free (a-CSi:H) and oxygen-bound (a-CSiO:H) individual layers deposited at different effective power or pulse period from tetravinylsilane and tetravinylsilane in a mixture with oxygen gas, respectively, by plasma-enhanced chemical vapor deposition operated in pulsed mode. XPS depth profiling using argon cluster ion beams was used to determine the atomic concentration of carbon, silicon, and oxygen in individual layers forming the multilayer nanostructures with a total thickness of about 100 nm. The XPS analysis revealed that the oxygen-free layers were oxidized due to post-deposition oxidation in the ambient air. Oxygen was even diffused in an oxygen-bound layer, which was confirmed by repeated XPS depth profiling within three months after multilayer deposition. The upper oxygen-bound layer at the multilayer surface behaved as a barrier reducing oxygen diffusion. The high energy-resolution XPS spectra (C 1s, Si 2p, and O 1s) were analyzed to gain more insight into bonding species formed in functionally nanostructured film. This detailed analysis showed that oxygen atoms, originating from the ambient air, were bound in oxidized (a-CSi:H) layers forming the same bonding states as those in as-deposited oxygen-bound layers.

4:40pm **TF+SS-TuA8 Studying Electron Induced Chemical Changes of Hafnium Oxide-Methacrylate EUV Photoresists with *In Situ* IR Spectroscopy and Model Flat Surfaces***, **Yasiel Cabrera**, E. Mattson, K. Oyekan, Y. Wang, Y.J. Chabal,* University of Texas at Dallas

New development in extreme ultraviolet (EUV) photolithography, using 13.5 nm photons, has brought us closer to a new era of device fabrication with sub-10 nm nodes. In the last decade, there has been many significant contributions to the development of EUV lithography, but limitations in photoresist development has made it difficult to implement the technology. Another significant challenge arises from the reality that EUV scanners are very expensive and limited for academia purposes, which ultimately slow down the process in understanding important mechanistic details for optimization of EUV resist materials. In this work, we emulate industrial EUV ionizing photons/events with low energy 90 eV electrons, which are believed responsible for inducing chemistry. Here, we are presenting results for nanoclusters resist based on hafnium-oxide core capped with methacrylic acid ligands (HfMAA). Using a combination of *in situ* infrared (IR) spectroscopy and density functional theory (DFT) calculations, we establish an atomic-scale mechanistic picture for each step of a photo-lithography process. To further understand the chemical changes leading to solubility switching, we have also developed a model surface system by translating the 3D structure considered in an HfMAA thin films (< 30 nm thick on SiO_2) to a 2D system comprised of a single methacrylic acid (MAA) monolayer grafted onto an ALD grown HfO_2 film. The model system allows us to explore three areas related to the nanocluster system: first IR spectroscopy shows that the model surface is a good representation of the HfMAA thin film by matching many of the IR modes observed; second, similar to HfMAA, 90 eV electron irradiation shows the formation of alkyl CH_2 groups on the surface, with the loss of carboxylate and C=C bonds in the MAA adlayer; third, by comparing with different metal-oxide surface (Al_2O_3 and TiO_2) and different carboxylate ligands (isobutyric acid (IBA), and hydroxybenzoic acid (OHBA)), we have demonstrated that analogous metal oxide/adlayer combinations can be used as a comparative tool to survey optimal combinations of organic and inorganic compounds for resist development by quantitatively evaluating the role of metal centers in inducing reactions.

5:00pm **TF+SS-TuA9 Photoactivated Molecular Layer Deposition of Fluoropolymer Thin Films***, **Richard Closser**,* Stanford University*; M. Lillethorup,* Radisurf Aps, Denmark*; D.S. Bergsman, J. Shi, S.F. Bent,* Stanford University

Recent developments of organic thin-film technologies have highlighted the need for deposition techniques which allow for a high degree of control over film thickness and conformality. Many methods, such as chemical and physical vapor deposition, have made substantial progress towards meeting those requirements; however, molecular layer deposition (MLD) may be the ideal candidate for future development. MLD is an organic vapor deposition technique that takes advantage of sequential, self-limiting surface reactions, analogous to atomic layer deposition (ALD), whereby thin-film polymers can be deposited with angstrom-level thickness control even onto high aspect-ratio features. There are inherent constraints, however, to the variety of chemistries available for MLD, due to its vapor-phase nature, which precludes the use of solvents and many catalysts. As a result, most MLD polymers contain heteroatom-type connectivities and do not include new carbon-carbon bonding moieties, thus preventing the formation of many of the most common commercially available polymers.

Here, we discuss a new approach to MLD, photoactivated molecular layer deposition (pMLD), a process which provides new pathways to forming carbon-carbon bonds. In pMLD, monomers are activated upon exposure to UV light to create metastable radicals, which are then reacted with alkenes in a step-wise polymerization. Self-limiting bifunctional precursors are chosen which limit the extent of homopolymerization while enabling layer-by-layer growth. In this work, an alternating hydrocarbon-fluorocarbon polymer was deposited via pMLD using bifunctional diiodofluoroalkanes and dienes. It was determined using ellipsometry that the deposition has a constant growth rate and displays saturation behavior. X-ray photoelectron spectroscopy (XPS) analysis indicates the formation of new carbon-carbon bonds. By using alternate monomer backbones, we show that the composition follows a nearly 1:1 monomer deposition ratio, an indication that homopolymerization is minimized. In situ XPS annealing shows the fluoropolymer exhibits high temperature stability up to 400 ºC, similar to a pure polytetrafluoroethylene polymer. The films also display chemical resistivity to a variety of solvents, acids, and bases. Elemental mapping using Auger electron spectroscopy confirms that the fluoropolymer film can be patterned using a UV photomask. We also show that the pMLD film can be used for ALD inhibition, blocking up to 100 cycles of Pt ALD. The strategy described in this work enables a new scope of applications for MLD, whereby carbon-carbon bonds are formed, greatly expanding the MLD toolbox.

5:20pm **TF+SS-TuA10 Sputter-Deposited Porous Coatings for Solid Phase Microextraction***, **Tuhin Roychowdhury**, D.I. Patel, M.R. Linford,* Brigham Young University

Solid Phase Microextraction (SPME) is 'green method' for isolating target analytes from complex matrices. It works by placing a coated fiber near a sample such that the molecules of interest can be selectively extracted and concentrated. These captured species are then released into a chromatograph for separation, identification, and quantification. Popular, commercial SPME coatings suffer from various drawbacks that include solvent incompatibility, low capacity, limited lifetime, etc. These problems are addressed by our new class of SPME fibers that offer extraordinary capacity, sensitivity, and speed. Our approach includes sputtering silicon onto fiber substrates to produce columnar structures. These porous silicon nanostructures are further oxidized leading to a high density of silanol groups on their surfaces. We have now demonstrated that both silanes and ultrathin PDMS layers can be deposited on these surfaces. These coatings can be produced in various morphologies and thicknesses by manipulating the sputter and deposition conditions. For example, refractory materials like carbon can also sputtered onto these fibers to create porous morphologies, which should be beneficial for chromatography. The surfaces and materials generated for SPME in this project have been characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), spectroscopic ellipsometry (SE), time-of-flight secondary ion mass spectrometry (ToFSIMS), and wetting . The performance of our 2 µm thick, porous, sputtered coatings has been compared to that of a thicker (7 micron) commercial coating. Our fiber consistently outperforms the commercial fiber, showing significantly higher capacity for higher molecular weight polycyclic aromatic hydrocarbons (PAHs). PAHs are a significant environmental pollutant due to their toxicity and carcinogenicity. These results are not the end of what is possible. Based on our work in this area we are convinced that further significant improvements in extraction efficiency and selectivity are possible.

5:40pm **TF+SS-TuA11 Interfacial Electron Transfer of Ferrocene Immobilized onto Indium Tin Oxide through Noncovalent Interactions***, **Caitlin Hanna**, J. Yang,* University of California, Irvine

Immobilization of molecular species onto electrode surfaces is a strategy for the modification of surface properties with molecular specificity. Attachment of molecular fuel forming catalysts to photovoltaic electrodes, for example, is a promising route to efficient solar fuel generation. Current attachment methods are synthetically difficult and can have adverse effects on the electrode performance. This report describes a non-covalent method for molecular immobilization onto indium tin oxide (ITO) surfaces. The fabrication, characterization, and electrochemical behavior of 1-pyrenylferrocene physisorbed onto ITO surfaces through π-π interactions is described. X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry confirm the attachment of 1-pyrenylferrocene to the surface and highlight the stability of the system for aqueous electrochemical applications. The electron transfer kinetics between the ITO electrode and non-covalently attached ferrocene are compared to the kinetics of covalently-bound ferrocene. The kinetic studies of electron transfer show that electron transfer is ten times faster for non-covalently attached ferrocene than for covalently attached ferrocene.

6:00pm **TF+SS-TuA12 Vapor Phase Infiltration of Polymers with Intrinsic Microporosity: Structure and Chemical Separation Performance***, **Mark Losego**, E.K. McGuinness, F. Zhang, R. Lively,* Georgia Institute of Technology

Over 10% of the world's energy consumption goes to separating chemicals via thermal distillation. Membrane-based separation can drastically reduce these energy and financial costs, but membranes must be carefully designed to meet performance and durability needs. Polymers of intrinsic microporosity like PIM-1 are emerging membrane materials of interest for industrial separations. These materials can be readily formed into films and/or fiber bundles for rapid chemical separation. However, PIM-1 swells in many solvents (e.g., ethanol) and can suffer from long-term porosity collapse. We have been investigating the vapor phase infiltration of these PIM-1 materials with inorganic constituents to improve performance and long-term stability. These studies have revealed a number of surprising observations including that these materials can be loaded to an excess of 30 wt% inorganics using a single VPI exposure dose despite no indication of chemical binding between the organic and inorganic constituents. We currently believe this loading is due to an intermediate binding state between the metalorganic precursors and the PIM-1's nitrile group. This binding state is sufficiently stable to withstand 2 days of inert gas purging, yet when exposed to an oxidant and removed from the reaction chamber no permanent chemical reactions between inorganic and PIM-1 can be detected by XPS, NMR, or FTIR. After infiltration, these organic-inorganic hybrid membranes show unprecedented performance for a PIM, fully capable of separating small molecules in ethanol solvents that should swell and collapse the polymer's pores.

Vacuum Technology Division
Room 203B - Session VT-TuA

IoT Session: Vacuum System Design and Automation & Flash Networking Session

Moderators: Julia Scherschligt, National Institute of Standards and Technology, Martin Wuest, INFICON

2:20pm **VT-TuA1 Vacuum Chamber Design and Fabrication.***, **Steve Greuel**,* Nor-Cal Products **INVITED**

The Vacuum Chamber Design and Fabrication presentation will provide insights and considerations for those who are involved with the design and specifications of vacuum chambers. Proper vacuum chamber design, materials, machining, welding and other processing fundamentals will be discussed, as well common pitfalls to avoid during the design phase.

3:00pm **VT-TuA3 The Importance of Vacuum Cleanliness in Semiconductor Process Control SEM Tools***, **Irit Ruach Nir**,* Applied Materials, Israel*; M. Eilon, K. Luria, G. Eytan,* Applied Materials **INVITED**

In the semiconductor manufacturing process, integrated circuits are formed by many layers, and hundreds of process steps are required to produce a single wafer. If any problem occurs at any step of the production process, a huge amount of defective products will be produced. Therefore, inspecting the wafers during the production process is essential in order to discover any problem and solve it as early as possible.

Scanning electron microscopes are playing an important role in process control and yield management of the semiconductors process. Defect review (DR) SEMs are used for defect identification, review and classification, enabling the semiconductor fabrication plant (fab) yield management system to identify failures or problems at an early stage in the process flow and to point on possible root cause. The Critical Dimension (CD) SEM is used to measure critical dimensions of the fine patterns formed on the semiconductor wafer, enabling verification of process quality. Since the SEM tools are in-line tools it is essential that they will not affect the scanned wafer.

Organic contamination is one of the main challenges in vacuum systems and hence in e-beam based metrology systems. Organic molecules adsorbed on the wafer surface during SEM inspection may cause yield loss in the following process steps or affect the CD measurement. In addition, with decrease in design rules the processes become more and more sensitive to organic contamination and therefore the ability to control vacuum cleanliness is crucial. In this paper, we will specify some of the challenges involved in the design of clean SEM based metrology tools, possible contamination sources and possible effects of such contamination molecules on the wafer.

4:20pm **VT-TuA7 Compact Ultra High Vacuum Systems for Applications of Cold Matter***, **Evan Salim**, S. Hughes, M.A. Perez, D.Z. Anderson,* ColdQuanta Inc. **INVITED**

Cold and ultracold states of matter offer tremendous potential to disruptively impact in the fields of timekeeping, inertial sensing, EM field sensing, and information science. Currently, however, the complexity of high-performing cold atom systems constrain them to laboratory environments. As the enabling technology matures these states of matter are beginning to make the transition from pure science to becoming critical engineering tools. For that transition to be successful, it is necessary for the building blocks of cold atom systems be simplified, stabilized, and ultimately commercialized. At the heart of all of these cold atom systems lies an ultra-high vacuum (UHV) package. In this talk we present on the progress towards miniaturized UHV technologies that support the specific requirements of atomic systems, such as high-quality optical access, non-magnetic structures, and exquisite control of local electromagnetic fields. Our approach takes advantage of compatible material systems, such as glass and silicon, to produce monolithic chambers that eliminate the need for flanges and similarly bulky components. We will also present on how these novel vacuum systems will enable future applications, including clocks and quantum computers, and will help to define a standard set of integrated UHV platforms for cold atoms.

5:00pm **VT-TuA9 Plasma Window as Vacuum Atmosphere Interface for Various Applications*, Ady Hershcovitch,*** Brookhaven National Laboratory **INVITED**

The Plasma Window is a novel apparatus that utilizes a stabilized plasma arc as an interface between vacuum and atmosphere or pressurized targets without solid material. In addition to sustaining a vacuum atmosphere interface, the plasma has a lensing effect on charged particles. The plasma current generates an azimuthal magnetic field, which exerts a radial Lorentz force on charged particles moving parallel to the current channel. With proper orientation of the current direction, the Lorentz force is radially inward. This feature can be used to focus in beams to a very small spot size, and to overcome beam dispersion due to scattering by atmospheric atoms and molecules

The best results to date have been the following:

1. Vacuum (pressure of ~ 10^{-6} Torr) was successfully separated from atmosphere and from a gas target pressurized up to 9 bar.

2. A 2 MeV proton beam was propagated from vacuum through the plasma window into atmospheric pressure with no measurable energy loss or beam degradation.

3. A 175 KeV electron beam was transmitted from vacuum through the plasma window to atmospheric pressure.

4. Successful transmission of X-rays from a light source to atmosphere.

5. Compatibility tests for transmission of electromagnetic radiation indicated that the plasma window does not generate electromagnetic interference, and that X-rays (away from resonance) are transmitted with negligible attenuation.

6. Electron beam welding in atmosphere (by an electron beam passing from vacuum through a plasma window) was accomplished with electron beams of unprecedented low power. Weld quality for the non-vacuum plasma window electron beam welding matched the quality of in-vacuum electron beam welding.

7. Internal gas stripper of ½ atmosphere helium confined by 2 plasma windows in accelerator vacuum.

Many industrial processes like electron beam welding and melting, as well as, ion material modification have low production rates due to required pumping time, and limits on the size of target objects. Utilization of the plasma arc as a window for targets removes these limitations and increases production rates. Other applications that can greatly benefit from plasma windows are those involving transmission of intense radiation or particle beams like high power lasers or deep ultraviolet photolithography sources, internal gas targets and beam dumpds. Plasma windows are practically completely transparent to high-energy particles and radiation, and unlike conventional windows, plasma windows are completely impervious to thermal damage.

5:40pm **VT-TuA11 Applications of IoT in Vacuum Technology*, Jacob Ricker*,** *J. Hendricks,* NIST

Automation has become a necessary tool for scientists as they are expected to do more with less time and money. NIST is currently utilizing IoT (internet of things) in several applications to evaluate and control processes that benefit from continuous monitoring while simultaneously freeing up staff time. The presentation will feature two examples to highlight how IoT is changing how we monitor sensors and process data for real-time automation of vacuum technology. First, NIST's utilization of IoT to automatically protect and monitor primary pressure standards, and second, the use of IoT to monitor encasements holding historical documents such as a draft of the emancipation proclamation in Lincoln's handwriting.

Primary pressure standards require continuous pumping and must be monitored as failures can cause water vapor to contaminate the ultra-pure vacuum systems and monometer fluids. Additionally, it can cause damage to expensive vacuum pumps and cause significant down time of the system. Microcontrollers and circuits were designed and constructed to monitor pressure in the system, rotation of the pump, and to control shutoff valves if necessary. Additional controllers monitor for cooling water failures to protect diffusion pumps from overheating and for compressed air failure which would disable the automated valves. All these systems work simultaneously and report issues back to the operator.

In collaboration with the Smithsonian, Library of Congress, National Archives, and other agencies around the country, NIST has worked to fabricate encasements that protect historical documents such as the Declaration of Independence, US Bill of Rights, and Emancipation Proclamation. All these encasements have featured sensors to monitor gas quality/stability; however recently IoT has enabled real-time monitoring of these readings to prevent operators from having to make manual readings of these sensors. The latest version of the encasement monitors Temperature, Humidity, O2 content, encasement pressure, and barometric pressure which are all reported and processed on cloud data storage. IoT has enabled instantaneous feedback and ensured these documents are preserved for future generations.

Exhibitor Technology Spotlight Workshops
Room Hall A - Session EW-TuAB

Exhibitor Technology Spotlight Session III
Moderator: Christopher Moffitt, Kratos Analytical Inc

4:00pm **EW-TuAB2 eSpectra, your Data, and your Collaborations***, Jessica Hoy,* AIPP/AVS

Are you looking for an easier way to analyze spectral data and share your results with your collaborators? Learn more about eSpectra, the new online platform where you can plot, compare and share your data in just a few clicks. Brought to you by AVS and AIP Publishing, eSpectra is the only interactive tool of its kind that lets you easily plot your data against peer-reviewed data, public data, or your team's data to better understand, analyze, and validate your results. Download and print plotted graphs, or save, share, and store your graphs and data in a secure environment. It includes XPS, AES, and UPS experimental techniques, with additional techniques planned for Fall 2018. Our Free Access and our Individual or Team Premium Access options support a range of research needs from academic to corporate. When you register, you receive a 30-day free trial of Premium Access. There will be 3 chances to win a $25 Starbucks® gift card at the session. If you're unable to attend, you can sign up anytime for free at eSpectra.aip.org.

Extending Additive Manufacturing to the Atomic Scale Focus Topic
Room Hall B - Session AM-TuP
Extending Additive Manufacturing to the Atomic Scale Poster Session

AM-TuP2 Laser Induced Formation of Eutectic Nanostructures in Al-Cu Powder for Additive Manufacturing*, Jonathan Skelton*, *C.V. Headley, J.A. Floro, J.M. Fitz-Gerald,* University of Virginia

With the emergence of additive manufacturing (AM) via laser powder bed sintering, design of the starting powders represents a critical area of interest, dictating the final properties of the AM components a large degree. The ability to design the nanoscale physical structure within powder particles in order to improve the final properties (optical, mechanical, thermal) remains a challenge. This research investigates the change in the eutectic microstructure of Al-Cu powders following laser irradiation. The initial powder alloy (gas atomized, Al-33wt%Cu) exhibited a variety of eutectic microstructures due to the varying solidification rates of particles within the gas atomized process. As-received powder was annealed at 450°C for 2 hours so as to create a uniform, Al+Al_2Cu two-phase structure with an interphase periodicity of about 2 µm. The original lamellar eutectic is broken down into a more irregular structure as part of the coarsening process. The powder, mounted on a glass slide and within an air ambient, is then subject to pulsed laser irradiation (wavelength = 248 nm, pulse duration 25 ns, fluence of 1.5 J/cm^2). Irradiation melted the particles, creating a new eutectic solidification structure with lamellar morphology. The interphase spacing was reduced to 30 nm, indicative of rapid solidification. Due to the lack of wetting or sintering between particles, it was concluded that each particle was melting and solidifying within its respective oxide shell. Though particles retain a largely spherical shape, many particles displayed a collapsed or partially “deflated” morphology after laser irradiation. The origin of the deformed morphology is not understood, but does not appear to be a phenomenon strictly associated with an instability imposed by the pulsed irradiation. It is suspected that the rapid growth and deflation of the oxide shell due to the thermal expansion of the Al-Cu particles may play a role. Samples were characterized by scanning electron microscopy (SEM), dual beam focused ion beam (DB FIB), and x-ray photoelectron spectroscopy (XPS). Support of the National Science Foundation through grants CMMI-1663085 is gratefully acknowledged.

Biomaterial Interfaces Division
Room Hall B - Session BI-TuP
Biomaterial Interfaces Division Poster Session

Moderator: Joe Baio, Oregon State University

BI-TuP3 Stimuli-responsive Thin Films made from Highly Methoxylated Citrus Pectin*, Zeinab Veisi,* *N. Alcantar, R. Toomey,* University of South Florida

We have used high-methoxyl citrus pectin polysaccharides to fabricate ultra-thin responsive coatings to be potentially implemented as elements of stimuli-responsive systems with diverse applications in drug delivery, tissue engineering, biomedicine, and etc.

Pectin is composed of a backbone chain structure of D-galacturonic acid units linked by α-1,4-glycosidic bonds. The carboxyl groups present in a polygalacturonic acid chain may exist as charged carboxyl acid groups or esterified with methyl groups. The ratio of methyl esters per total number of carboxyl groups is defined as the degree of esterification (DE). Low-methoxyl pectin (DE<50%) can be cross-linked in the presence of divalent ions such as Ca^{2+} ions. High-methoxyl pectin exhibits weak affinity for Ca^{2+} cations due to the lower charged carboxyl group content challenging their Ca^{2+}-induced cross-linking.

Herein, thin coatings of high-methoxyl citrus pectin were fabricated as surface-attached hydrogel networks by spin-casting solutions of pectin onto a solid surface followed by Ca^{2+} induced crosslinking. The cross-linking was performed by introducing the cross-linker (Ca^{2+}) in a poor solvent for pectin to eliminate water in the cross-linking process. Cross-linking the coatings in a non-solvent ensures that the coatings remain intact by preventing dilution of the pectin chains. However, the Ca^{2+} ions freely diffused into and cross-linked the pectin to form robust coatings. Using this strategy, pectins with up to 70% esterification were cross-linked. Generally, high-methoxyl pectins do not cross-link in the presence of calcium unless at high pectin concentrations.

The coatings prepared in this manner demonstrated a volume-phase transition induced by temperature. The responses of coatings were assessed by characterizing their swelling behaviors using ellipsometry and ATR-FTIR to provide insights into the nature of the transition. Our findings show that at temperatures below approximately 35 ˚C, the coatings were hydrophilic. At higher temperatures, the coatings expelled water and collapsed giving rise to distinctive de-swelling profiles. The hydrophilic/hydrophobic transition was driven by dehydration of methoxyl groups whereas water remained bound to the carboxylate groups. It was also observed that the response of the coatings can be tuned by adjusting temperature, degree of cross-linking, and pH of the surroundings to induce a desired response. Our finds show that thin films of the high-methoxyl pectin polysaccharides can be employed for establishing responsive surfaces with tunable responses suitable for the pharmaceutical and biotechnology industries.

BI-TuP4 Fluorescent DNA Nanosphere Barcdoe System by Rolling Circle Amplification for Tumor Cells Detection*, SW. Han,* ***JongBum Lee,*** University of Seoul, Republic of Korea

Nucleic acid-based nanotechnologies have been developed with the base pairing property and applied to numerous bioengineering fields of study. As a novel engineering material, DNA has been used to fabricate nanostructures from simple 2D structures to complex 3D structures. With this development of DNA nanoarchitecture, enzymatic replication technique has been also attracted as a new strategy for building nucleic acid-based nanostructures. Here, DNA nanosphere (DNANS) is fabricated by rolling circle amplification (RCA) and coated with antibodies for target cells detection. DNANS can be applied as a barcode system which can distinguish the tumor cells by recognizing tumor-specific protein. As a proof of concept, the capability for target detection of DNANS barcode system was demonstrated. This target-specific antibody-coated DNANS suggests a new route for the simple and selective recognition of cancer cells.

BI-TuP7 Vapor-Deposited Porous Polymers for the Fabrication of Giant Lipid Vesicles*, Nareh Movsesian,* *M.T. Matthew Tittensor, G. Dianat, N.M. Malmstadt, M. Gupta,* University of Southern California

Giant unilamellar vesicles (GUVs) are cell-sized biomimetic model membranes useful for examining membrane properties and building artificial cells. Hydrogel-assisted rehydration is an emerging technique to form GUVs under physiological conditions at high yields circumventing the shortcomings of traditional techniques such as electroformation and gentle hydration. Herein we present porous negatively charged poly (methacrylic acid-co-ethylene glycol diacrylate) *(xPMAA)*membranes fabricated using an unconventional solvent-free initiated chemical vapor deposition (iCVD) technique and utilized as hydrogel substrates for vesicle formation. Physicochemical properties of the hydrogel substrates such as morphology and crosslinking density are controlled by iCVD process parameters. Zwitterionic and charged lipid mixtures are applied on hydrogel membranes as thin lipid films and subsequently swollen in an aqueous hydration buffer. Here we show that vesicle yield and size are controlled by the morphology, the density, and the charge of the polymer. Our findings show that high hydrogel porosity and reduced electrostatic interactions between the polymer and the lipid are preferred for vesicle formation.

BI-TuP8 Developing a pH Responsive Hydrogel for the Encapsulation of Poly(ethylene glycol) 3350*, Phuong Anh Nguyen*[1]*, *B. Matheson, D. Cuylear, H.E. Canavan,* University of New Mexico

Colorectal cancer (CRC) is the second leading cause of cancer-related deaths in the United States. The most reliable screening method of CRC is a colonoscopy which requires a 4-Liter poly(ethylene glycol) electrolyte lavage solution (PEG-ELS) for preparation. Two in five patients are non-compliant to their colonoscopy schedules, with many patients who abstain reporting refusal due to significant discomfort associated with this preparation. Furthermore, there are distinct gender differences in the tolerance of PEG-ELS in male and female populations. We hypothesize the differences in clinic are a result of cytotoxicity effects of PEG. PEG is approved by the FDA for use in medical devices, and has been recognized for many years as a biocompatible/bioinert polymer but few studies have truly studied the short-term and long-term effects of high concentrations of PEG on multiple cell lines. We have developed a pH responsive hydrogel to control the release of PEG – reducing adverse effects associated with colonoscopy preparations. The hydrogels have been characterized using

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[1] **National Student Award Finalist**

NMR, FTIR, and XPS to ensure chemical identity, rheometry to assess the stiffness/robustness of the hydrogels in varying environments, and SEM and other techniques to confirm uniformity of size. Biocompatibility testing of exposure to increasing PEG concentrations over a period of 3 hours, 6 hours, 12 hours, 24 hours, and 48 hours shows PEG is biocompatible to mammalian cell lines in low concentrations, and in fact, increases their growth and viability. At higher concentrations, however, PEG is cytotoxic to cells. Although it would be difficult to get to toxic levels of PEG in the body in a single dose, current uses of PEG should be re-evaluated due to possible adverse cumulative effects due to the cytotoxicity effects seen *in vitro.* Further directions of this work will evaluate the pH responsiveness of our hydrogel formulation to deliver PEG *in vitro* and *in vivo,* and assessment of the cellular response to the hydrogels using mammalian cells specific to the gastrointestinal system of humans, as well as imaging analysis to envision their penetration.

BI-TuP9 Hemocompatibility of the Endexo™ Fluoro-oligomeric Surface*,* *Bill Theilacker,* Medtronic*; J. Ho, J. Swenor,* Interface Biologics*; M.F. Wolf, J.L. Kalscheue, S. Thinamany,* Medtronic*; S. Ubl,* medtronic

Blood represents one of the most complex biochemical systems in living organisms. As a result, the design of medical device materials is often tailored to reduce platelet adhesion and activation, protein adsorption, and thrombus formation. With roughly 50% or more of Medtronic products contacting vascular tissue, medical device materials that show evidence of biocompatibility with blood (aka 'hemocompatibility') are of high interest. The Endexo™ surface treatment from Interface Biologics is asserted to show improved hemocompatibility through the action of low molecular weight fluoro-oligomeric additives that bloom to the surface and reduce or inhibit blood platelet activation and procoagulant protein formation. Incorporating Endexo technology into materials is straightforward and does not change the mechanical or functional properties of the underlying medical device.

Through a collaborative effort, we examined the IBI fluoro-oligomeric additive added to a common copolyester base polymer used in blood-contact applications and evaluated the platelet and coagulation protein activating capacity. Tritan™ polyester (Eastman) was formulated with several different concentrations of Endexo™ fluoro-oligomeric additive. The surface chemistry of the samples was characterized by Scanning Electron Microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). An in vitro vacuum test tube model developed at Medtronic was employed to asses hemocompatibility. Complete blood count analysis, platelet activation (via ELISA immunoassay for platelet plasma protein βTG), and coagulation protein formation (via ELISA immunoassay for the thrombin coagulation protein indicator TAT) was evaluated in the exposed blood.

The Endexo™ surface modifying agent appeared to show improved interaction with blood platelets. Similar favorable performance as assessed by TAT and βTG indicators of hemocompatibility may suggest a viable avenue for incremental improvement in the hemocompatibility of blood contacting devices and device materials. Surface analysis results show the Endexo formulated materials are modified with F-rich chemistry with no change in surface morphology. Medical devices that show improved performance in *in vitro* studies of hemocompatibility have potential to show improved performance in the *in vivo* clinical setting.

BI-TuP10 High Performance Dopamine Sensor Based on Field-Effect Transistor (FET) with H uman Dopamine Receptor Integrated-Multidimensional Conducting Polymer Nanofiber*,* *Jinyeong Kim,* *S.J. Park,* Korea Research Institute of Bioscience and Biotechnology (KRIBB), Republic of Korea

Dopamine (DA) has been studied in the field of nervous and cardiovascular systems. Abnormal levels of dopamine is an indicator of neurological disorders, resulting in Alzheimer's and Parkinson's diseases. Therefore, dopamine is a clinically useful diagnostic sign and requires a novel approach with high sensitivity, selectivity and a rapid response. Various sensors have been developed, such as high-performance liquid chromatography (HPLC), mass spectroscopy, and spectrophotometry. However, they are limited by their high cost, low sensitivity, and variable label response.

The field-effect transistor (FET) has been used in the development of diagnosis for several decades. It is gated by changes of charge carrier density in the channel induced by the binding of target molecules, leading to high-performance biosensors. In addition, the FET platform has attracted due to their low cost, easy operation, fast response, label-free operation, parallel sensing as well as high sensitivity.

In this article, we introduced a high performance dopamine sensor based on FET assay. Multidimensional carboxylated poly(3,4-ethylenedioxythiophene) (MCPEDOT) NFs membrane was utilized as the conductive channel of sensor in the FET system. Interestingly, it provided high performance sensing due to enhanced interaction from high surface area and gate-potential modulators. Moreover, hDRD1, G protein-coupled receptors (GPCRs) as the recognition elements, was first expressed in Escherichia coli and modified with the surface of MCPEDOT NFs, leading to high selectivity. As a results, the hDRD1−MCPEDOT NF-based FET exhibits a rapid real-time response (<2 s) with high dopamine selectivity and sensitivity performance (approximately 100 fM).

BI-TuP11 Detection of B-type Natriuretic Peptide in Human Serum Based on Flexible Biosensors and Data Analysis Methodology*,* *Xinruo Yi,* *A. Khalaf, R. Gunasekeran, M.H. Yun, M. Akcakaya,* University of Pittsburgh*; Y.Z. Zhang, S. Marc, N. Petroni,* UPMC

The demand on using biosensor during clinical diagnosis to detect the heart failure (HF) becomes increasing at market. B-type natriuretic peptide (BNP), as we know, is a hormone in response to stretching resulting from increased ventricular blood volume. The detection of BNP plays an important role in HF and various diagnosing cardiovascular diseases. Hence, it is important to alarm abnormal BNP levels and to monitor BNP changes appropriate to the diagnostic ranges for an HF event. In particular, BNP levels in human blood range from < 100 ng/l for normal humans to 101 ~ 1000 ng/l for HF patients. Finding BNP level will help the physician make decisions on whether the patient should be admitted to hospital or discharged.

We present a simple, high yield, low-cost and label-free method based on a two-dimensional (2-D) flexible polyaniline (PANI) biosensor along with ultra-sensitivity and specificity for biomarker detection. The 2-D PANI film which was chemically synthesized in a facile and controllable way had high surface-to-volume (S/V) ratios and showed good semiconducting properties. In order to prepare our biosensor, first, we performed surface modification using 1-ethyl-3-(3-dimethyaminopropyl) carbodiimide (EDC), and N-hydroxysuccinimde (NHS) to fix the monoclonal antibodies onto the 2-D PANI film. Second, the 2-D PANI film was treated by using non-target protein like bovine serum albumin (BSA) to block the free sites on the surface and further avoid getting noise signals. After that, our label-free biosensor for the detection of BNP is ready for the test. The detection of BNP in real human blood becomes complicated by the precipitation of red blood cells which will bind with the BNP antibody and block them to get the position of BNP antibody near biosensor surface. Instead, serum samples from patients with heart failure, obtained directly from the University of Pittsburgh Medical Center (UPMC) after separating the red blood cells from the whole blood by centrifugation, were tested.

In this work, we did the mixed blind test with two healthy samples (healthy sample) and two patient samples (with high BNP concentration). In addition, we used various approaches including electrical analysis, standard deviation method, principle component analysis (PCA), quadratic discriminant analysis (QDA) and linear discriminant analysis (LDA) to successfully identify these blind samples, which could be used to determine whether the patient has HF or not.

BI-TuP12 Characterizing Hetero-oligomer of Amyloid-beta and Alpha-synuclein with Bio-AFM*,* *Eun Ji Shin,* *J.W. Park,* Pohang University of Science and Technology, Republic of Korea

Alzheimer's Disease (AD) and Parkinson's Disease (PD) are neurodegenerative diseases resulting in progressive degeneration or death of neuron cells. These are associated with the aggregation of peptides, 'amyloid-beta (Aβ)' and 'alpha-synuclein (α-syn)'. It is believed that Aβ and α-syn oligomers are intermediates in the fibril formation, and both oligomers and fibrils are primarily responsible for the pathogenesis. Further study showed that rate of the oligomerization (or aggregation) increases when Aβ and α-syn co-exist, and the co-existence causes the diseases even worse. It is very likely that hetero-oligomers could be formed, but presence and structure of the hetero-oligomers have not been elucidated.

Herein, we employed atomic force spectroscopy with a liquid cell to characterize the hetero-oligomers generated in vitro. For comparison, homo-oligomers were prepared separately. In particular, antibodies recognizing N-terminal of Aβ and N-terminal of α-syn were conjugated at AFM probes, and the specific interaction between the antibodies and surface of the oligomers was followed. After adsorbing the oligomers on mica surface, a tip tethering Aβ antibody was used to get high resolution force maps of a target oligomer, and subsequently another tip tethering α-syn antibody was brought to the same target for the examination. The overlaid map revealed that specific unbinding events with respect to two different antibodies were observed within an oligomer, and it holds for all sizes under investigation. Because homo-oligomers were not observed at all, it can be said that formation of hetero-oligomers is strongly favored. It is intriguing to note that the percentage of recognizing pixels for α-syn increases in comparison with the α-syn homo-oligomer, suggesting a different mode of aggregation for the hetero-oligomerization. We believe that such structural information helps to understand the relationship between the misfolded proteins and the pathogenesis in brain.

BI-TuP13 Creation of de novo Nucleic Acid Binding Disordered Proteins using the Thermally Responsive Behavior of Elastin-like Polypeptides*, **Telmo Diez**, G.P. Lopez, N.J. Carroll,* University of New Mexico

Intrinsically disordered proteins (IDPs) are dynamic polypeptides used by eukaryotic cells in cell signaling, transcription, and chromatin remodeling functions are frequently employed in packaging and un-packaging of nucleic acids (NAs). Elastin-like polypeptides (ELPs) are biosynthetic biopolymers that have similar structural features to natural IDPs. Importantly, ELPs condense to form coacervates above a lower critical solution temperature (LCST). In this research, we focus on the combination of thermally responsive ELPs with natural nucleic acid binding domains to create promising responsive engineered protein constructs. In this study, we show how an ELP comprising nine positive charges from eight lysine interspersed within the chain is capable of interacting with NAs above its LCST. We characterize the amount of DNA captured by ELP and we use microfluidics to form aqueous microdroplets containing the ELP and fluorescent DNA to visualize DNA capture within ELP coacervate spheres via fluorescence microscopy. We characterize the thermodynamic binodal phase boundary (i.e. in the temperature-concentration dependent phase diagram) of the ELP[Office3] [#_msocom_3] /NA mixture to resolve the ELP volume fraction within the coacervate to predict the optimal temperature to maximize DNA capture. Finally, we combined this ELP with smaller RRM and RGG domains that bind nucleic acids found in natural FUS protein, a common NA binding protein that plays a role in genomic integrity.[Office4] [#_msocom_4] RRM is a 70 amino acid domain found to bind promiscuously to nucleic acids, and RGG is a 100 amino acid long domain rich on arginine and glycine found to be essential in the RRM interactions with nucleic acids. These studies have implications for, and yield insights into, the tailoring of engineered protein constructs that bind nucleic acids with predictable behavior and controlled release that could have many applications in gene therapy and other areas of bionanotechnology.

Spectroscopic Ellipsometry Focus Topic
Room Hall B - Session EL-TuP

Spectroscopic Ellipsometry Focus Topic Poster Session

Moderator: Tino Hofmann, University of North Carolina at Charlotte

EL-TuP1 An In situ Spectroscopic Ellipsometry Study of Cerium Oxidation*, **Wayne Lake**, P. Roussel,* AWE, UK

Cerium is an electropositive metal and will be covered by an oxide film. X-ray Photoelectron Spectroscopy (XPS) measurements have shown the oxide film to be composed of the trivalent oxide at the metal interface and the tetravalent dioxide at the oxide gas interface. Furthermore, in ultra high vacuum the dioxide film is thermodynamically unstable with respect to the cerium metal substrate and reduces to the trivalent oxide. The XPS technique is limited due to the small depth probed, therefore, to follow cerium oxidation reaction with oxide films greater than 10 nm spectroscopic ellipsometry offers a better technique of choice. At the AWE the spectroscopic ellipsometer is attached to an in situ film growth chamber on the XPS spectrometer. The problem with spectroscopic ellipsometry arises from the data interpretation. Spectroscopic ellipsometry modelling of a substrate with a single oxide film is easily achieved. However, when two oxides of different oxidation state are formed this presents a more difficult challenge to model.

Starting from sputter cleaned cerium substrate, the sample is heated and exposed to oxygen and the reaction is followed by using in situ spectroscopic ellipsometry. The substrate model is determined from the first data points in the data set prior to exposing the sample to oxygen. This work addresses how we determine a suitable model to interpret the spectroscopic ellipsometry data where two oxides are present.

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EL-TuP2 In-situ Multi-wavelength Ellipsometric Monitoring of the Reactive Sputter Deposition of WO_x Films*, **Ned Ianno**, G. Kaufman, C. Luth,* University of Nebraska-Lincoln*; C. Exstrom, S.A. Darveau,* University of Nebraska at Kearney*; B. Johs,* Film Sense

Thin films of WO_x where x<3 have a range of applications as sensors, while amorphous WO_3 thin films have been employed as the precursor films for the growth of WSe_2 and WS_2 films. The WO_x films have been deposited by reactive sputtering in an Oxygen/Ar ambient, while the WO_3 films have primarily deposited by thermal evaporation although reactive sputter deposition has also been reported. Based on the literature and the work reported here the reactive sputter deposition of WO_x is very dependent on plasma bombardment during growth, and the voltage applied to the sputter gun, as well as the more straightforward parameters such as pressure, flow rate and substrate temperature. In view of this we have performed a 2-level factorial survey of the deposition parameter space associated with the reactive sputter deposition of WO_x films where we varied the O/Ar flow rate ratio, total chamber pressure, substrate temperature and sputter gun magnetic configuration to provide a more fundamental understanding of the deposition of WO_x films. A critical part of this work is the use of in-situ multi-wavelength ellipsometry (data acquired at 4 wavelengths in the visible spectrum: blue, green, yellow, and red) to monitor the growth process where we will show the sensitivity of the ellipsometric data to stoichiometry of the film, both during deposition and post deposition annealing.

EL-TuP3 Mid-infrared Optical Constants of InAsSb Alloys and Bulk GaSb*, **Pablo Paradis**, S. Zollner, R. Carrasco,* New Mexico State University, Department of Physics*; J. Carlin, V. Dahiya, A. Kazemi, S. Krishna,* The Ohio State University, Department of Electrical and Computer Engineering

Antimonides are attractive materials for mid-infrared detectors and emitters, because they form a direct band gap, which can be tuned from 0.1 to 0.7 eV. For the design and modeling of such devices, the optical constants of these materials must be known. We present results of Fourier-transform infrared (FTIR) ellipsometry measurements of bulk GaSb and doped and undoped InAsSb alloys with different compositions. Doped and undoped layers of InAsSb alloys were grown on GaSb substrates by MOCVD. Their optical constants were determined using two different methods. First, we fitted the data as a sum of oscillators representing the free-carrier and interband optical response, which allows a physical interpretation of the results. Second, we expanded the dielectric function into a sum of Kramers-Kronig consistent B-spline polynomials, assuming thicknesses obtained from the growth parameters. In the doped layers, a free-carrier reflectance band can clearly be seen in the spectra, while the undoped layers show an absorption increase at the band gap. The 10% Sb samples are lattice matched and the 44% Sb samples are lattice mismatched leading to some strain inhomogeneity in the samples. This can be seen in the dielectric function of these samples. In the doped samples, we analyze the optical conductivity obtained from parametric oscillator fit. We pay attention to the plasma frequency term in our parameters to describe the behavior of the conductivity in doped vs undoped layers.

EL-TuP4 Temperature-dependent Ellipsometry and Thermal Stability of Ge2Sb2Te5:C Phase Change Memory Alloys*, **Cesy Zamarripa**, N. Samarasingha, F. Abadizaman, R. Carrasco, S. Zollner,* New Mexico State University

Ge2Sb2Te5 (GST) compounds are phase change memory alloys. At temperatures above 425 K, they are crystalline, forming a metastable rocksalt (T>425 K) or a stable hexagonal crystal structure (T>525 K). Heating the alloys above their melting point, followed by rapid cooling to room temperature (on a nanosecond time scale) forms an amorphous phase, where the resistivity is at least three orders of magnitude higher than in the crystalline phase.1 This enables their use as rewritable optical recording media. Carbon doping allows tuning of the amorphous to crystalline transition temperature. In this work, we performed temperature-dependent spectroscopic ellipsometry measurements of as-deposited (amorphous) GST alloys in high vacuum from 300 to 800 K in 25 K steps, at an incidence angle of 70°. The samples were held approximately three hours at each temperature. We used two different instruments, a J.A. Woollam Fourier-transform infrared ellipsometer with ZnSe windows from 0.07 to 0.7 eV and a J.A. Woollam VASE ellipsometer with quartz windows from 0.5 to 6 eV. The GST layers were about 750 nm thick and deposited on singleside polished Si wafers covered with 400 nm of SiO2. The original room-temperature measurements show two sets of interference fringes below 1 eV, due to the two different films present on the wafer. The SiO2 absorption bands at 0.15 eV are clearly visible. The GST layers are transparent in the infrared without any lattice vibration features, due to the large mass of the constituent atoms. The absorption rises rapidly at 1 eV towards a broad maximum at 1.7 eV and then drops smoothly towards the UV. The dielectric function of the as-deposited films is featureless, as expected for an amorphous layer. The ellipsometric spectra are essentially unchanged between 300 and 400 K, showing an absorption threshold near 1.1 eV. At 425 K, this threshold suddenly drops to 0.7-0.8 eV, where it remains constant up to 675 K. The dielectric function is featureless at all energies and never displays any sharp features expected for a crystalline material. No amorphous to crystalline phase transition can be observed in the optical spectra. Spectra above 700 K show only the interference oscillations from the SiO2 oxide layer. Apparently, the GST film has evaporated.

Acknowledgments: CMZ acknowledges support from the New Mexico Alliance for Minority Participation. This work was supported by NSF (DMR-1505172).

1. E.M. Vinood, K. Ramesh, and K.S. Sangunni, Sci. Rep. 5, 8050 (2015).

In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic
Room Hall B - Session MM-TuP

In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic Poster Session

MM-TuP1 In-situ Low Energy Electron Microscopy at Near Ambient Pressures*, **Thomas Schulmeyer,*** SPECS Surface Nano Analysis GmbH

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, 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. As a new development, the technical capabilities of LEEM and PEEM have been extended toward near ambient conditions by developing a special objective lens concept and sample chamber geometry. This enables the analysis of materials and devices under near ambient conditions and even in situ during operation. For this a Laser heater allows for sample temperatures up to 800°C during the measurements. The technical realization will be presented in detail. Furthermore experimental results will be shown on Graphene, Silicon under Nitrogen atmosphere. First results from real surface reactions will be discussed.

MM-TuP2 NanoESCA III: Recent Progress and Applications*, M. Merkel, N.B. Weber, M. Escher, T.-J. Kühn,* FOCUS GmbH, Germany*; **Marten Patt,*** Scienta Omicron GmbH, Germany

During the last years essential progress has been made in developing the technique of energy filtered photoemission electron microscopy (PEEM). Different approaches of imaging energy filtering have been introduced and developed more and more.

One of the most essential achievements was in 2003 the invention [1] and design of the imaging double energy analyser (IDEA), an aberration compensated band pass filter. This PEEM dedicated energy filter became the core element of the NanoESCA III instrument. Its unique design allows for high quality imaging of band pass filtered PEEM images at UV light excited threshold energies for e.g. work function mapping up to hard x-ray energies (HAXPEEM) [2] for bulk sensitive measurements.

Both the real and the momentum space of a sample can be imaged by direct switching in between both modes. The latter so called momentum microscopy, acquiring the full band structure from a microscopic sample region of interest, becomes a more and more popular alternative to the common ARPES set-up using a single hemispherical analyser. Besides elimination the major component of the analyser's spherical aberration, the tandem arrangement also largely retains the time structure of the electron signal, unlike a single hemispherical analyser which can be helpful with time resolving experiments.

We will show some recent applications [3] and instrumental set-ups taking advantage of these possibilities.

[1] D. Funnemann, M. Escher, European Patent EP 1 559 126 B1, US patent US 7 250

599 B2

[2] Patt et al., Rev. Sci. Instrum. 85, 113704 (2014)

[3] see e.g.: Ming-Wie Chen et al., npj 2D Materials and Applications (2018) 2:2 ; doi:10.1038/s41699-017-0047-x

Manufacturing Science and Technology Group
Room Hall B - Session MS-TuP

Topics in Manufacturing Science and Technology Poster Session

MS-TuP1 Formation of High Entropy Film for Cutting Tool by Magnetron Sputtering*, **Ki Buem Kim,*** Sejong University, Republic of Korea*; T. Choi,* Sejong university, Korea, Republic of Korea*; H.Y. Lee,* Korea Institute of Industrial Technology, Republic of Korea*; J.K. Lee,* Kongju National University, Republic of Korea*; Y.S. Kim,* Sejong University, Republic of Korea*; Y.K. Park, K.S. Kim, S.I. Jeong,* YG-1 Co. LTD, Republic of Korea

Hard coating application is effective way of cutting tool for hard-to-machine materials such as Inconel, Ti and composite materials focused on high-tech industries which are widely employed in aerospace, automobile and the medical device industry also Information Technology. In cutting tool for hard-to-machine materials, high hardness is one of necessary condition along with high temperature stability and wear resistance. In recent years, high-entropy alloys (HEAs) which consist of five or more principal elements having an equi-atomic percentage were reported by Yeh. The main features of novel HEAs reveal thermodynamically stable, high strength, corrosion resistance and wear resistance by four characteristic features called high entropy, sluggish diffusion, several-lattice distortion and cocktail effect. It can be possible to significantly extend the field of application such as cutting tool for difficult-to-machine materials in extreme conditions. Base on this understanding, surface coatings using HEAs more recently have been developed with considerable interest due to their useful properties such as high hardness and phase transformation stability of high temperature.

In present study, the nanocomposite coating layers with high hardness on WC substrate are investigated using high entropy alloy target made a powder metallurgy. Among the many surface coating methods, reactive magnetron sputtering is considered to be a proper process because of homogeneity of microstructure, improvement of productivity and simplicity of independent control for several critical deposition parameters. The N2 is applied to reactive gas to make nitride system with transition metals which is much harder than only alloy systems. The acceleration voltage from 100W to 300W is controlled by direct current power with various deposition times. The coating layers are systemically investigated by structural identification (XRD), evaluation of microstructure (FE-SEM, TEM) and mechanical properties (Nano-indenter).

MS-TuP3 Trace Level Detection of Gas Impurities Using Atmospheric Pressure Ionization Mass Spectrometry*, **Gregory Thier,*** Extrel CMS

Analysis of trace amounts of impurities in gases is crucial for applications such as Environmental Monitoring, Catalysis, Semiconductor Production, and others. Atmospheric Pressure Ionization Mass Spectrometry (APIMS) provides a technique for detecting and monitoring very low level impurities in these gases. Atmospheric pressure ionization is a chemical ionization method used in a variety of spectrometry and chromatography analyses. APIMS uses gas-phase ion-molecule collisions at atmospheric pressure for ionization and detection of trace components and impurities. Using an Extrel® VeraSpec™ Trace API Mass Spec, detection limits of less than 5 parts per trillion (ppt) have been observed. By optimizing energy of ion-molecule collisions, these low detection limits have been observed in samples with complex mixtures. This method is used for research applications of gas characterization, but has also been applied to real-time monitoring of gases.

MS-TuP4 Novel Safe Approach to Process Gas Delivery*, **Richard Elzer,*** Entegris*; K.W. Olander,* Retired co-founder of ATMI Corp

The history of high pressure toxic gases is riddled with safety events, actual injuries and deaths as well as near misses, some reported and many not report. In some cases, the risk profile of these gases has driven organizations to adopt low % gas mixtures that may impact process results.

Technology has been developed to store and deliver pure undiluted (neat) gases in a manner that drastically reduces the risk, with multiple technologies implemented. In one implementation, gas is stored in a gas cylinder and delivered subatmospherically.

In another implementation, gases are stored at high pressure but delivered from the gas cylinder subatmopherically. Both neat gases as well as specialty gas mixtures may be delivered from this gas package.

In a third implementation for processes requiring delivery pressures above atmospheric pressure, gases are stored at high pressure but delivered from the gas cylinder at 100psi. Again, both neat gases as well as specialty gas mixtures may be delivered from this gas package.

We will present the technologies and provide insights

improved process results

Removal of excess impurities

More deliver grams of target gas per cylinder

Insurers and Regulatory Bodies' view and preference for the safe package

Unique classifications by the US DOT

Cylinder sizes and configurations available for various applications

MS-TuP5 Advanced Characterization to Support Development of Next Generation Phosphors*, **Vincent Smentkowski**, R. Davis, J. Murphy, A. Setlur, M. Butts, J. Lu,* General Electric Global Research Center*; W. Beers,* Current by GE

Over the past decade significant improvements have been made in phosphor technology resulting in improved brightness, color gamut, lifetime and reliability in order to meet market demands for next generation LED Lighting and display technologies. Over 20 billion K_2SiF_6:Mn^{4+} containing LEDs have been sold into the display industry in less than 4 years under GE RadiantRED™ Technology.

Achieving these demands require the development of accurate, and reproducible methods to characterize and monitor the microstructure, surface, subsurface, and bulk chemistry of the phosphor powders (including dopants such as Mn^{4+}). In this poster we will highlight a sub set of the novel analytical techniques we developed with an emphasis on the analysis of dopants and their three dimensional distribution in the phosphor powders. The criticality of sample handling and preparation for accurate analysis will be addressed.

Plasma Biology, Agriculture, and Environment Focus Topic
Room Hall B - Session PB-TuP

Plasma Biology, Agriculture, and Environment Focus Topic Poster Session

PB-TuP1 Detection of Metallic Ions in Solution Using Optical Emission Spectroscopy of Plasma Driven by Bipolar Pulsed Power Sources*, **Ching-Yu Wang**, C.-C. Hsu,* National Taiwan University, Taiwan, Republic of China

Detection of metallic ions in solution using optical emission spectroscopy in plasmas offers advantages including simultaneous detection of multiple elements, minimization of cross-element interference, and rapid detection. In this work, plasma ignited in metallic-salt-containing-solution using bipolar pulsed DC power is studied. The goal is to understand how the modulation of the bipolar pulsed power influences the plasma optical emission of metallic elements. A power source that provides asymmetric bipolar voltage pulses of a duration between 10 µs to 100 ms with an amplitude up to ±1 kV is used. Plasma is ignited inside the gas-phase formed in the solution. The gas phase composes of water vapor, oxygen, and/or hydrogen through joule heating and/or electrolysis. The plasma behavior and therefore the optical emission are greatly influenced by the width, polarity, and amplitude of the bipolar pulses. Voltage and current probe are used to conduct electrical analysis; optical emission spectrometer and photo multiplier tube are used to perform time-averaged optical emission spectroscopy and time-resolved emission intensity, respectively.

While using repetitive 7500µs-widelow voltage pre-pulses followed by 100 µs-wide 600 V pulses to ignite plasma in solution consisting of 0.1 M HNO_3, 500 ppm Pb, and 250 ppm Na, we observe a low peak current with the application of the pre-pulse. The intensities and ratios of H, Pb, and Na emission lines are varied with different polarity and amplitude of the pre-pulse. The above observations show the modulation of the voltage pulses greatly influences the plasma behavior and therefore its optical emission. This work provides an effective way to tailor the plasma behavior and its optical emission, which could potentially be used as a strategy to obtain more reproducible and sensitive detection of metallic ion in water for analytical purposes.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room Hall B - Session PC+AS+BI+EM+NS+PB+SS-TuP

Processing and Characterization of Gas-Liquid, Solid-Liquid, and Gas-Solid Interfaces

PC+AS+BI+EM+NS+PB+SS-TuP1 Operando Photoelectron Spectroscopic Study of Copper-based Oxide Semiconductor Interface with Water*, **Pitambar Sapkota**, S. Ptasinska,* University of Notre Dame*; A. Cabrera,* Instituto de Física, Pontificia Universidad Católica de Chile

The quest for suitable semiconductor photoelectrodes to build efficient and stable photoelectrochemical (PEC) cells for solar water splitting is continually growing in the material sciences and solar energy community. Along with good stability in aqueous media, such photoelectrodes should have suitable band-edges and band-gap energies properly matching both the water oxidation-reduction potential and the solar spectrum, respectively. Copper-based oxide semiconductors are promising candidates fulfilling these criteria, but little is known about the interfacial properties of these compounds with H_2O under operational conditions. Therefore, knowledge of their surface dynamics and interfacial reactions under realistic conditions is essential to improve our understanding of water-splitting mechanism, as well as to increase the stability and efficacy of PEC devices. Ambient pressure X-ray photoelectron spectroscopy was used to characterize the semiconductor surface and study the chemical reactions occurring at the interface under the reaction conditions. In this study, thin films of $CuFeO_2$ and $CuFe_{1-x}Ga_xO_2$ composites were exposed to various H_2O pressures and temperatures. Water interactions with the Cu-based oxide surface and the electronic structures of the surface atoms were evaluated from the Cu 2p, Fe 2p, C 1s and O 1s photoemission spectra to identify surface species newly formed.

PC+AS+BI+EM+NS+PB+SS-TuP2 Interfacial Water in Silicon-based Catalytic Motors*, **Jordi Fraxedas**, K. Zhang, B. Sepulveda, M.J. Esplandiu,* Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Spain*; X. Garcia, J. Llorca,* Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Center in Multiscale Science and Engineering. Universitat Politècnica de Catalunya, Spain*; V. Perez-Dieste, C. Escudero,* Alba Synchrotron Light Source, Spain

Self-propelled motors that can harvest chemical energy from their surroundings to convert it in mechanical energy are at the cutting edge of nanotechnology for their appealing applications in e.g., environmental remediation and nanobiomedicine. A full understanding of the propulsion mechanism is crucial to improve their performance and controllability. Recently, a simple motor made of silicon and a noble metal that can operate with visible light has been developed [1]. The photoactivation mechanism and consequent motion is essentially based on the formation of electron/hole pairs. The holes are strong oxidizing agents for the species in the fluid producing protons and the electrons can diffuse towards the metal surface and participate in the counterpart reduction reaction. As a result, a gradient of proton concentration is formed in the fluid which builds-up an electric field driving the motion of the fluid through electro-osmosis. A mechanism that competes with the electro-osmotic process is based on diffusion-osmosis and is triggered by the redox decomposition exclusively at the metal surface and is not light responsive. We have recently shown that it is possible to enhance/suppress one mechanism over the other by tuning the surface roughness of the micromotor metal. Thus, the actuation mechanism can be switched from light-controlled electrokinetics to light-insensitive diffusio-osmosis by only increasing the metal surface roughness [2].

We have recently performed near ambient pressure photoemission studies of Pt/Si micromotor surfaces activated by oxygen plasma in water atmosphere at the NAPP endstation of the CIRCE beamline at the ALBA synchrotron near Barcelona. We have used p-type silicon substrates with one half covered with a Pt film with a thickness of about 50 nm grown by both e-beam and sputtering deposition. The results reveal a chemical gradient at the Si/Pt edge with a reduction of the Pt species. The analysis has to carefully consider the photochemical reactions induced by the combined action of the impinging beam and the water condensed at the surfaces. The beam induced damage evolves in two regimes: an initial preferential reduction of Pt4+ species and then the reduction of Pt2+ species, which increases the metallic character of the surface.

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PC+AS+BI+EM+NS+PB+SS-TuP3 Chiral Modification of Oxide-Supported Pt Surfaces: An in-situ ATR-IR Study*, Yufei Ni,* University of California, Riverside*; F. Zaera,* University of California, Riverside

The synthesis of enantiopure compounds is of great significance to the designing of pharmaceuticals and agro products. Possible methods for the manufacture of enantiopure chemicals include the separation of racemic product mixtures and reactions with other chiral chemicals, but perhaps the most promising procedure is the use of enantioselective heterogeneous catalysis. Chiral modification of catalytically active metals such as Pt and Ni is believed to be the most feasible approach to produce chiral heterogeneous catalysts. In this context, the use of cinchona alkaloids-modified Pt for the hydrogenation of activated ketones has drawn particular attention in the past few decades. A better understanding of how these chiral modifiers work to bestow enantioselectivity is still a prerequisite for the design of such catalysts.

In this project, we have used attenuated total reflection infrared absorption spectroscopy (ATR-IR) to investigate the details of the adsorption of such cinchona-alkaloid chiral modifiers on the Pt surfaces of supported catalysts in situ at the liquid-solid interface. It was determined that adsorption can be only observed after H_2 pretreatment of the catalyst. A comparison study in terms of adsorption strength was carried out using not only cinchona alkaloids such as cinchonidine and cinchonine but also simpler alternatives such as (R)- or (S)-(−)-1-(1-naphthyl) ethylamine (NEA), naphthylmethyl amine, and dimethyl naphthyl ethylamine.The adsorption strength of the different modifier molecules was found to be quite different among those compounds. This is illustrated by the fact that quinoline can displace s-NEA from Pt but not vice versa, for instance, and by the observation that when Pt is exposed to a solution containing both quinoline and s-NEA only the quinoline's signature peaks can be detected by ATR-IR spectroscopy. The ordering of the modifiers studied in terms of adsorption strength was found to correlate with their ability to chirally modify the Pt catalyst during the hydrogenation of unsaturated aldehydes.

Finally, it was found that NEA bonds to the metal through the nitrogen atom of its anime moiety, and not through the aromatic ring as commonly believed.

PC+AS+BI+EM+NS+PB+SS-TuP4 Wettability Behaviour of Synthesized Carbon Nanospheres and its Application as a Photocatalyst*, Sonal Singhal,* *A.K. Shukla,* IIT Delhi, India

Superhydrophobic and superhydrophilic surfaces have been widely investigated due to their diverse range of applications such as self-cleaning, microfluidic application in biotechnology, corrosion, Anti-reflecting coatings and microelectronic mechanical system etc. Here, a facile chemical vapour deposition method is reported for the synthesis of carbon nanospheres (CNSs). Henceforth, the morphology of as-synthesized sample is characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray diffraction (XRD), Raman spectroscopy and FTIR spectroscopy are used to determine the phase purity, chemical composition and presence of chemical bonds on the surface of synthesized CNSs. TEM and SEM results reveal the presence of CNSs with a diameter ranging from 50 nm to 400 nm. Raman spectroscopy confirms the presence of disordered carbon and low graphitization, which are also confirmed by TEM and XRD results. Optical properties of as-synthesized CNSs is investigated by UV-Vis spectroscopy and photoluminescence. Wettability behaviour of as-synthesized carbon nanospheres is investigated by contact angle measurements. CNSs shows a water contact angle of 152^0, which confirms the fabrication of superhydrophobic carbon nanosphere surface. After the proper explanation of wettability behaviour, it also discusses the application of as-synthesized CNSs as a photocatalyst. As it is well known, catalyst enhances the chemical reaction rate without changing its properties. Therefore, various kind of catalysts has been developed for the purpose to enhance the catalysis for environmental applications. Among different materials, carbon-based materials are widely used as a catalyst support due to their excellent properties. Considering these facts, the degradation of an organic pollutant under UV light is discussed here using CNSs.

PC+AS+BI+EM+NS+PB+SS-TuP5 Thermally Driven Solid-solid Li^+ Transfer into Nanostructured TiO_2*, Tiffany Kaspar,* *T. Varga,* Pacific Northwest National Laboratory*; D.A. Shapiro,* Advanced Light Source, Lawrence Berkeley National Laboratory*; A. Martinez, Y. Shin, K.S. Han, M.-S. Lee, S. Thevuthasan, V. Murugesan,* Pacific Northwest National Laboratory

Due to their good chemical stability, strong oxidation capability, and desirable lithium electrochemical activity, nanostructured titanium dioxide (TiO_2) anode materials have received considerable attention recently. Decreasing the particle size to 10-20 nm can increase the electrochemical capacity to 200-300 $mAhg^{-1}$. Furthermore, nanostructured TiO_2 anodes are non-toxic and would be suitable for cost effective mass production. Among the rutile, anatase, and brookite polymorphs of TiO_2, anatase nanoparticles have shown the best Li ion insertion properties and maximum reduction, indicating increased Li ion intercalation into the material. Here, we have synthesized 10-20 nm anatase TiO_2 nanoparticles and contacted them with solid Li- bis(trifluoromethanesulfonyl)imide (LiTFSI) as a function of temperature to understand the chemical and structural effects associated with thermally driven solid-solid Li^+ transfer to, and intercalation in, TiO_2 nanoparticles. We have used a combination of x-ray photoelectron spectroscopy (XPS), Ti L-edge scanning transmission x-ray microscopy (STXM), Raman spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy to gain a fundamental understanding of the structural evolution of TiO_2 nanoparticles during Li^+ intercalation. Our results indicate that thermally driven solid-solid Li^+ transfer to TiO_2 has occurred, and altered the TiO_2 structure at the edges of the agglomerated nanoparticles.

Plasma Science and Technology Division
Room Hall B - Session PS-TuP

Plasma Science and Technology Division Poster Session

PS-TuP2 N_2/H_2, O_2 and NF_3 Dissociation Percentages in a Remote, Low Frequency, High Density Plasma Source*, Yingliang Zhou,* *H. Li, V.M. Donnelly,* University of Houston*; J. Chiu, X. Chen,* MKS Instruments, Inc., Pressure and Vacuum Measurement Group

Remote plasmas are drawing increasing attention for applications including chamber cleaning, chemical vapor deposition (CVD), surface modification and isotropic etching. The process is purely chemical in nature, with no surface damage from ion bombardment. The dissociation and recombination rates in the plasma source determine the reactive species fluxes delivered to the downstream chamber. The presentation will focus on measurements of percent dissociation of source gases commonly used in chamber cleaning and flowable CVD processes. Mixtures of N_2/H_2, O_2, and NF_3 feed gases with Ar were delivered to the plasma at 400 sccm total flow rate and pressures of 0.4-4.0 Torr. The purely inductive, low frequency (400 kHz), toroidal plasma source (MKS Instruments) operates at a power density of 5 – 50 W/cm^3. Radical densities and feed gas dissociation percentages in the plasma were measured by UV-visible optical emission spectroscopy (OES), combined with Ar actinometry. Effluents from the plasma source flowed into a downstream chamber that was equipped with a Deuterium lamp and a VUV spectrometer, for absorption spectroscopy measurements. The dissociation of O_2, NF_3 and N_2/H_2 gases in the plasma source will be compared to those measured downstream as a function of added Ar, total flow rate, discharge current, relative electron density and other plasma parameters.

PS-TuP3 Thermal Atomic Layer Etching of Silicon and Silicon Nitride Using an Oxidation and "Conversion-Etch" Mechanism*, Aziz Abdulagatov,* *S.M. George,* University of Colorado at Boulder

The thermal atomic layer etching (ALE) of silicon (Si) and silicon nitride (SiN) was performed using an oxidation and "conversion-etch" mechanism. In this process, the Si or SiN surface is oxidized to a silicon oxide layer using O_2 or ozone. The silicon oxide layer is converted to an Al_2O_3 layer using trimethylaluminum (TMA). The Al_2O_3 layer is fluorinated by HF to an AlF_3 layer prior to the removal of the AlF_3 layer by ligand-exchange using TMA. Si ALE was studied using silicon-on-insulator (SOI) wafers and SiN was examined using LPCVD SiN films. These investigations were performed in a warm wall reactor with a hot sample stage. *In situ* spectroscopic ellipsometry was employed to monitor the thickness of both the Si or SiN film and the silicon oxide layer during ALE.

These studies observed that the Si and SiN film thickness decreased linearly with number of reaction cycles while the silicon oxide thickness remained constant. Using an O_2-HF-TMA reaction sequence, the Si ALE etch rate was 0.4 Å/cycle respectively at 290°C. This etch rate was obtained using static reactant pressures of 250, 1.0 and 1.0 Torr, and exposure times of 10, 5 and 5 s, for O_2, HF and TMA, respectively. The order of the reactant sequence affected the Si etch rate. Changing the reactant sequence from O_2-HF-TMA to O_2-TMA-HF reduced the etch rate from 0.4 to 0.2 Å/cycle at 290°C. Comparable etching rates were observed using ozone instead of O_2 as the oxidant. Comparable etching rates were observed for SiN ALE under similar reaction conditions. The Si and SiN ALE etch rates decreased with process temperature. An oxide thickness of ~10 Å remained after ALE at 290°C. However, this oxide thickness could be removed by sequential TMA and HF exposures without influencing the underlying silicon film.

These new thermal Si and SiN ALE processes are expected to yield isotropic etching. Thermal Si and SiN ALE should be useful in advanced semiconductor fabrication. Thermal Si ALE could also be utilized for atomic-scale polishing and cleaning of silicon surfaces. In addition, there may be applications in other areas such as silicon-based optoelectronics, photonics and MEMS fabrication. Thermal SiN ALE could be utilized in a broad spectrum of IC applications where SiN commonly used as an etch stop and diffusion barrier.

PS-TuP4 Annihilation Kinetics of Plasma-induced Electronic Defects in Semiconductor Materials*, S. Nunomura, **Isao Sakata**, K. Matsubara,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

In semiconductor devices such as transistors, memory, solar cells, and light emitting devices, the electronic defects strongly impact on the device performance and reliability. These defects are often generated during the device fabrication, in which plasma processing technology is widely used for deposition, etching and implantation. To remove the defects in the devices, a annealing treatment is usually performed. However, some defects remain in the devices, and they deteriorate the device performance. The reduction of these residual defects is required, and thus it is important to understand the annihilation kinetics during the annealing period.

We studied the annihilation kinetics of electronic defects in hydrogenated amorphous silicon (a-Si:H). The electronic defects were generated by photon irradiation and plasma treatment. The annihilation of defects during the annealing is observed by in-situ photocurrent measurement [1-2]. An increase in the photocurrent reflects the annihilation of the defects. From the time evolution of the increasing photocurrent, we obtained the characteristic time, τ, and an Arrhenius plot is prepared to determine the activation energy.

From the experiments, we find the following [3]. (i) The time evolution of the photocurrent exhibits the stretched exponential behavior, indicating the dispersive nature of a-Si:H. (ii) An Arrhenius plot shows an exponential decay of 1/τ vs 1/T, verifying defect annihilation due to the thermal activation. Here, T is the annealing temperature. (iii) The activation energy is different, depending on the origin of defect generation. It is smaller for the defects generated by plasma treatments, compared with that of the defects induced by the photon irradiation. (iv) The exponential prefactor is different between the UV and VUV photon-induced defects. The details of the experimental setup, results and discussion will be given in the presentation.

This work was supported by JSPS KAKENHI (Grant Number 18K03603 and 15K04717) and NEDO.

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PS-TuP5 High efficiency Magnetic Induction Plasma Source for Remote Plasma Removal Process*, **TaeSeung Cho**, S. Park, D. Lubomirsky,* Applied Materials

Selective material removal by using remote plasma becomes an indispensable process for 3D structures of semiconductor. In selective material removal process by remote plasma, the wafer process regime is completely isolated from the plasma source by perforated metal plates such as showhead. The radicals generated by electrical discharge pass through the perforated metal plate, while the charged particles cannot pass through. Thus, in the wafer process regime, the specific radicals from the remote plasma react with the target material to be removed from the wafer. Since the charged particles are screened by the plate, the damages by energetic charged particles can be drastically reduced. Therefore, the plasma source for remote plasma removal process should have features of (1) efficient radical generation with higher dissociation rate and (2) less charged particle leakage to wafer process regime.

Magnetic induction plasma concept is being used for lighting bulbs as well as Tokamak fusion reactor for several decades. Especially, the magnetic induction lighting and its driving electronics is being optimized for many years. Since the magnetic induction lighting doesn't have any electrode inside the bulb there's no particles from the electrode sputtered by energetic ions. In addition, magnetic induction plasma source as an inductively coupled plasma has higher dissociation rate compared to typical capacitively coupled plasma. Thus, introducing the magnetic induction lighting and its driving technologies to remote plasma removal process would make removal process more efficient and reliable with reduced cost of ownership.

Prototype chamber for magnetic induction plasma source for remote plasma removal process was assembled with standard KF flanges that could be brought off the shelf. To generate stable plasma, we modified the commercial electronic ballast. We introduced initial plasma generation concept to avoid the ignition failure which was one of the most common issue of magnetic induction plasma source. For preliminary study with the electrical and optical diagnostics, Ar+N_2 plasma was successfully generated/modulated in the chamber by using the ballast with wide operating pressures from 50mTorr to 200Torr.

PS-TuP6 Aspect-ratio and Line-edge Fluctuation Controlled Nanolithography using Poly(styrene-*b*-Dimethylsiloxane) and Amorphous Carbon Layer*, **JiSoo Oh**, G.Y. Yeom,* Sungkyunkwan University, Republic of Korea

Of the various alternative lithography technologies, direct self-assembly (DSA) patterning technology using block copolymer (BCP) has received great attention due to excellent pattern resolution, process simplicity, low cost, and long-range ordering (good scalability).

Polystyrene-block-polydimethylsiloxane (PS-*b*-PDMS) with high Flory-Huggins interaction parameter (χ) have been extensively studied because they provide ultra-fine patterning and improved pattern quality. However, due to the preferential segregating property of PDMS in air and PS interface, it is disadvantageous to vertical orientation and it is difficult to fabricate BCP patterns with high aspect ratio (HAR)

Here, we will introduce the process of effectively pattern transfer by inserting an amorphous carbon layer (ACL) between the PS-*b*-PDMS BCP patterns and the underlying silicon substrate. In this study, we have overcome limitations of PS-*b*-PDMS BCP patterns with low aspect ratios by developing an etch selectivity close to infinity using plasma etch process. The PDMS patterns of various shapes could be fabricated into lamellar, rod, hole pattern with HAR by pattern transfer to ACL due to high etch selectivity plasma process. Also, line edge roughness (LER) and line width roughness (LWR) was improved due to the plasma trimming effect.

PS-TuP7 Development of A Low-Cost ZnO Nanorods-Based Gas Sensor with an Integerated Microplasma Generation Unit for Ethanol Sensing*, **Sz-Yun Lin**, F.-H. Huang, C.-C. Hsu,* National Taiwan University, Taiwan, Republic of China

ZnO-based materials have been widely used as the gas sensing elements. The major limitations for this type of materials are the need to operate in high temperature or the requirement of the annealing step for fabrication or re-condition.

In this work, we developed a ZnO nanorods–based gas sensor integrated with a microplasma generation unit (MGU) that allows for detection of ethanol vapors at room temperatire. This device consists of a specially-designed electrode set was fabricated using toner transfer method. This allows for the operation of microplasma generation mode(MGM) and gas sensing mode(GSM). After the fabrication of the 3-electrode set, ZnO nanorods was grown by hydrothermal method for 24 hours between two electrodes. ZnO-nanorods was first treated using the plasma for 10 minutes by sensing test. By proper connection of the electrodes, the device can be operated in GSM, which allows for ethanol vapor sensing test by measuring the resistance across the ZnO nanorods. The sensor is capable to detect a wide range of ethanol vapor, from 25 to 20000 ppm. In addition, the sensor shows excellent recyclibility after repetitatively testing for over 30 cycles. We will also show that the plasma treatment of the ZnO nanorods serves as the regeneration of the sensing materials after the nanorods expose to humid air and loses their functionality for ethanol sensing.

This newly-developed integrated device offers a novel route for the dvelopment of sensing devices that allows for plasma treatment of sensing materials in-situ and on-site.

PS-TuP8 Development of a Plasma Generation Device Integrated with a Piezoelectric Spray to Detect Metal Ions in Solution*, Ting-Ting Pan, S.-Y. Lin, C.-C. Hsu,* National Taiwan University, Taiwan, Republic of China

In this work, we develop a system that contains a plasma generation device, a piezoelectric spray, and a spectrometer to detect metallic ions in solution. The plasma consists of a needle and a copper sheet as the anode and the cathode respectively. This plasma is driven by a homemade high voltage module that delivers 3 kV DC and is powered by a 5 V commercial portable power bank. The plasma is ignited in ambient air without the need of any purging gases. The mist of metal-ion-containing solution is sprayed to the plasma. The optical emission of the plasma is analyzed using a spectrometer for metallic element analysis. Such an arrangement allows for analysis of solutions with a wide range of electrical conductivities.

It is shown that the addition of a ballast resistor in series of the high voltage module effectively limits the current and plays an important role for metal detection. Without the ballast resistor, no metallic emission line is observed, despite of the fact that the plasma shows very bright emission. With the use of a ballast resistor of proper resistance, plasma appears to be more stable and clear Na and Pb emission lines are observed when a solution containing 1000 and 10000 ppm of Na and Pb, respectively, is spray to the plasma. We also observe that the gap between the electrodes is very critical for plasma characteristics. With a gap smaller than 0.5 mm, the plasma exhibits stable (DC) IV waveforms, while it shows self-pulsing characteristics with a gap greater than 0.5 mm.

We will show the progress toward the ultimate goal of this work: development of a system to detect metal ions in solution by integrating the plasma and spray devices with a home-made low cost spectrometer, and control the system using a Raspberry pi, a portable computer. Such an integrated system is fully functionalized and standalone and allows for simultaneous detection of multiple metal ions using plasma spectroscopy.

PS-TuP9 Development of a Light-weight System for Detection of Metal Ions in Solutions Using Plasma Spectroscopy*, Ching-Yu Su*, *S.-Y. Lin, C.-C. Hsu,* National Taiwan University, Taiwan, Republic of China

This work presents the development of a light-weight system that allows for simultaneous detection of multiple metallic elements in solution using plasma spectroscopy. This system consists of a pin-to-surface-type plasma, driven by a home-made high voltage module, and an atomizer to spray test solution into plasma. The optical emission of the plasma is analyzed using a spectrometer. Such an arrangement allows for detection metallic elements in solution with wide range of electrical conductivity of the solution by analyzing the optical emission of the plasma. A stainless steel pin and a copper sheet serve as the anode and the cathode, respectively, of the plasma. This plasma operates under atmospheric pressure in ambient air. The high voltage module delivers 3 kV DC to ignite the plasma and is powered by a 5-V commercial portable power bank. The atomizer is a piezoelectric spray. The power source of this spray is connected in series with a bipolar junction transistor (BJT), which is driven by a function generator to modulate the on and off of the spray. When the metallic element-containing solution is sprayed to the plasma, metallic emission can therefore be acquired.

We have observed that the spray frequency and duty greatly influence the plasma behavior and therefore its optical emission. Proper modulation of the spray is the key to generate stable plasmas with clear metallic emission. When the spray is set at 1 Hz with 50% duty using solution with 1000 and 10000 ppm of Na and Pb, respectively, clear metallic Na and Pb emissions are observed. We will further analyze the temporal-resolved optical emission to better understand the interaction between the mist and the plasma.

Finally, we will also demonstrate the use of a Raspberry Pi, a low-cost and credit-card-sized computer, to synchronize the spray and the plasma, and its integration with a homemade low cost spectrometer to develop a standalone and fully-functional device for detection of metallic elements in solution.

PS-TuP10 Inductively Coupled Plasma Reactive Ion Etching of Nanometer-scale Patterned Copper Thin Films using Alcohol-based Gases*, Jinsu Ryu*, *E.T. Lim, D.W. Park, C.W. Chung,* INHA University, Republic of Korea

Copper has been known as the next-generation interconnect materials in the metallization layer beyond the ultra large scale integration. Recently, the conventional aluminum interconnect materials needs to be replaced by copper which has many advantages compared to aluminum: high conductivity, less susceptible to electromigration, and lack of hillocks formations. Copper thin films could not be patterned by the previous patterning techniques of photoresist masking and plasma etching that had been used with great success with aluminum. The inability to plasma etch the copper films called for the development on new etching technique. At last, it lead to a unique patterning process referred to as an additive patterning, also known as a 'Damascene' or 'dual-Damascene' process by analogy to a traditional technique of metal inlaying. However, as the critical device dimensions keep shrinking, the thickness of copper interconnect also should be decreased. This shrinkage in the copper thickness cause several issues in the copper patterning, which contain the increase in the resistivity of copper interconnect due to the increase in the resistivity of barrier layer and the change in grain size. There were many etching studies on the copper thin films using halogen-containing gases (Cl_2, HBr), hydrogen, and some organic materials, and all of their results were not satisfactory to apply to the copper patterning.

In this study, we will introduce an etching process of copper thin films using high density plasma etching in alcohol-based gases. The etch characteristics such as etch rate and etch profile will be presented as a function of gas concentration. Then the systematic parameter variation will be performed to improve the etch profiles. Finally, the etch mechanism will be investigated using X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS). In addition, the plasmas properties will be analyzed using optical emission spectroscopy (OES) and Langmuir probe.

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PS-TuP11 Etch Characteristics of Nanometer-scale Patterned Cu Thin Film Using Pulse- modulated RF Source Plasma*, Euntaek Lim*, *J.S. Ryu, C.W. Chung,* INHA University, Republic of Korea

The critical dimensions of the semiconductor devices have been shrunk for better performance and functionality. As the minimum feature length keeps decreasing, the aluminum metal electrodes and wiring can not be used anymore and the need to use copper wiring instead of aluminum is increasing. Copper has very low resistance and high electromigration resistance, so the copper thin films is known as an excellent interconnect material compared to aluminum although the copper is more expensive than aluminum. In order to apply copper films into the interconnect, the pattering and etching process of copper films should be developed. Up to date, the studies on etch characteristics of copper thin films were performed using Cl_2, HBr, and H_2 gases but the satisfactory results were not obtained.

In this study, the pulse-modulated RF plasma etching of copper thin films has been introduced to achieve good etch results such as proper etch rate and good etch profile compared to those by the conventional continuous wave (CW) plasma etching which can produce low etch selectivity, etch residues, and poor etch profiles. This modulated plasma can provide the specific plasma conditions modified by special matching system that can change on-off duty ratio of 13.56 MHz RF power and frequency on the specific duty ratio. Currently, no good etch gases have been known to etch copper thin films. In this research, etching characteristics of copper thin film masked with nanometer-scale patterns was investigated in carboxylic acid using pulse-modulated inductively coupled plasma reactive ion etching (ICP RIE). The effects of on-off duty ratio and frequency of pulsed plasma on the etch characteristics of copper were examined.

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PS-TuP12 Etch Characteristics of Magnetic Tunneling Junction Materials by Using Noble Gas and Hydrogen*, SooGang Kim*, *K.C. Yang, Y.J. Shin, D.I. Sung, G.Y. Yeom,* Sungkyunkwan University, Republic of Korea

As next generation non-volatile memory device, spin transfer torque magnetic random access memory (STT-MRAM) is one of the prospective memory devices. But anisotropic etching of magnetic tunneling junction material (MTJ) is vey difficult especially in nano-scale. Ar ion beam etch (IBE) not only has low etch selectivity but also induces sidewall re-deposition. Even though tilted ion beam can remove deposited materials at sidewall, a shadow effect restricts the effective removal of deposited materials in nano-scale pitch size. Some chemical reactive ion etching (RIE) can improve problems of Ar IBE, but they show other problem such as low selectivity, corrosion and chemical damage to magnetic materials.

In this study, MTJ materials were etched by using H_2, Ne, Ar and Xe inductively coupled plasma (ICP) and observed their etch characteristics. The nano-scale patterned MTJ material sample which is composed of CoPt(10nm), MgO(1nm), CoFeB(10nm) with W hardmask was used for comparing etch profiles with re-deposition. The results show that H_2 and Ne etch showed better etch profile and higher etch selectivity of MTJ materials over W than those with Ar. With Xe, etch selectivity was lower than the other gas, even though Xe showed an anistropic profile. Also using the vibrating sample magnetrometer (VSM), we compared saturated magnetic moments (Ms) to identify magnetic degradation. The patterned sample etched with Ne and Ar showed similar Ms, which means no significant magnetic degradation when using Ne.

PS-TuP13 Particle Temperature Histories in a Tubular Low Temperature Plasma Reactor: Relevance to the Synthesis of Amorphous Metal Alloys,

N.B. Uner, ***Elijah Thimsen,*** Washington University in St. Louis

The nonequilibrium environment of low temperature plasma (LTP) allows it to incorporate a significant amount of specific free energy to materials with which it is in contact. It has been shown recently that LTP is capable of synthesizing materials that are far away from equilibrium, as in the case of hyperdoped silicon nanocrystals [1]. Furthermore, LTP can also process pre-synthesized materials in such a way that the material is pushed far away from equilibrium, as demonstrated with in-flight size focusing of polydisperse aerosols [2]. However, examples on the transformation of materials with equilibrium atomic structure to materials with non-equilibrium structure are scarce. In this work, we propose that the distinct nanoparticle (NP) temperature histories in tubular LTP reactors can be utilized to transform crystalline metals into amorphous metals. Spatial characterization of an Ar plasma in a capacitively coupled tubular reactor revealed the existence of a zone with sharply elevated ion density and gas temperature in the vicinity of the powered electrode. Theory suggests that such an intense zone would heat NPs to temperatures above 1000 K, and rapid cooling would follow as NPs leave the zone. In the characterized reactor, an aerosol processing scenario was simulated, where pre-synthesized crystalline NPs were sent into the LTP. Copper-zirconium (CuZr), which is a well-established glass former and is of interest for low temperature electro-catalysis applications, was taken to be the particle material. Calculations showed that the temperature history of a NP is strictly dependent on diameter, and on the intensity of the zone. CuZr melted in the intense zone, and subsequent cooling of the melt in the low intensity plasma downstream lead to quenching rates on the order of 10^5 K/s, all while particles maintaining a unipolar negative charge. Quenching rates of this magnitude are known to be sufficient to arrest an amorphous atomic structure [3].

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PS-TuP15 Easy Synthesis of Hybrid Laterally or Vertically Patterned Hydrophobic/Hydrophilic Surfaces using a Dielectric Barrier Discharge,

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The quest for obtaining smart materials with combined surface properties is driven by their many potential applications. Whereas the surface science community can now easily synthesize (super)hydrophilic or (super)hydrophobic surfaces, there is nowadays a specific interest for having stable surfaces where some spots are hydrophobic and some are hydrophilic, leading for instance to controlled chemistry at the hydrophilic part, leaving the hydrophobic part unchanged (this is particularly useful for biomedical applications where controlled adsorption of biological molecules can be requested)[1]. Similarly, for antibiofouling applications in marine environment, having layers alternating in depth an hydrophilic/hydrophobic behavior may lead to lower shell adsorption[2]. This type of multilayers coating can also find applications in the manufacturing of water filtration membranes[3].

In this research, we present a simple approach for synthesizing such patterns using a combination of two precursors, namely propargyl methacrylate (precursor for hydrophobicity) and acrylic acid (precursor for hydrophilicity) injected in a dielectric barrier discharge (DBD) operating at atmospheric pressure. A thin PVC mask is used for the surface patterning of the coating. Various amounts of the two precursors are injected in the DBD, which runs with argon as the main operating gas. These two precursors can indeed lead to coatings exhibiting contact angles varying from 140° to 15°[4]

The samples are characterized by secondary ion mass spectrometry (SIMS), both in static and dynamic mode, X-ray photoelectron spectroscopy and water contact angle. Despite the strong similarities between the two precursors, SIMS unambiguously show alternating in-depth composition of specific fragments. Similarly, water contact angle (with a reduced water drop size) shows that surface patterning is easily obtained by DBD, with contact angles of ~130° in hydrophobic areas and ~25° in hydrophilic areas. An alternate approach, consisting in exposing selected areas of the hydrophobic coating to an oxygen containing plasma, leads to angle of ~130° and ~17°, respectively. Such patterns are stable with time, opening the route for potential applications.

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PS-TuP16 Plasma-based Approach to Driving an Amorphous-To-Crystalline Phase Change in MoS_2 Grown on Polymers,

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The ability to grow high-quality, continuous 2D transition metal dichalcogenides (TMDs) on polymer substrates is a prerequisite for commercial flexible devices based on these materials. Molybdenum disulfide (MoS_2) is a promising 2D semiconductor due to its relatively high charge mobility and a direct band gap of 1.8 eV coupled with optical transparency and high mechanical flexibility. Recently, magnetron sputtering from pure TMD targets, such as MoS_2 and WS_2, was used for growth of amorphous precursor films at room temperature on polydimethylsiloxane substrates. *Ex situ* laser annealing after film growth was then used to drive an amorphous-to-crystalline phase change. While successful, the phase change was limited to the area defined by the beam diameter. Rapid, large scale, *in situ* methods would be an attractive alternative to meet the demands for commercial scale manufacturing.

In this work, we discuss the development of a plasma-based approach to driving the crystallization of few-layer, amorphous MoS_2 on polymers. The amorphous MoS_2 was deposited, via magnetron sputtering of MoS_2 targets, on polydimethyl siloxane (PDMS) substrate**s**. The films were then exposed to electron beam generated plasmas produced in pure and dilute argon backgrounds to drive crystallization. The use of electron beam generated plasmas are attractive since they are both scalable to large areas and deliver a large ion fluence with kinetic energies as low as a few eV. The ion energies can be raised using DC or RF biasing, allowing the system to be tuned to deliver the energy required to drive the phase transition but limit etching and damage to monolayer films. The treated films are characterized using Raman, XPS, and Kelvin probes and those results will be discussed in terms of operating conditions such as treatment times, operating gas mixture, and ion energy. This work was partially supported by the Naval Research Laboratory base program.

PS-TuP17 Atmospheric Plasma Deposition of Vanadium Oxide Thin Coatings on Cold and Heated Substrates,

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Atmospheric plasma deposition of vanadium oxide thin coatings on cold and heated substrates

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Vanadium oxides present interesting applications in thermochromic devices, electronic components, optoelectronics sensors, battery electrodes and catalysis. They can be synthesized by chemical vapor deposition (CVD) [1], or by magnetron sputtering [2]. In this research, we report, to the best of our knowledge, the first synthesis of vanadium oxide with a reactive atmospheric dielectric barrier discharge. This approach allows the direct synthesis of oxide layers on a wide variety of substrates, starting from an organometallic precursor in the vapor phase. Vanadium(V) oxytriisopropoxide vapours were injected in a DBD operating with argon as the main plasma gas. Variable quantities of the precursor and of oxygen (from 50 mL/min to 100 mL/min), operating as secondary reactive gas, were introduced in the discharge, and the plasma power was varied from 40 W to 60 W.

The coatings were deposited at room temperature, or, thanks to a new home made internal heating device, at higher substrate temperatures (ranging from 373 K to 573 K). Some coatings were post-annealed in air at 573 K.

The samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy and Infrared Spectrometry, in the IRRAS mode, and the electrical characteristics of the plasmas were studied by a high voltage probe. It is shown that the plasma power decreases with the introduction of oxygen, but remains virtually unchanged when the precursor is injected. Although, according to XPS, a significant amount of carbon still remains embedded in the final coating in the normal conditions of operation, typical IR bands for V_2O_5 at 1020 cm^{-1} and 850 cm^{-1} were observed for samples prepared with 50 mL/min of oxygen flow and at 300°C of sample temperature. This is confirmed by the oxidation state of vanadium (V5+), as observed by the XPS peak at 517.2 eV. The oxidation state seems to change with the conditions of the synthesis, starting from +5 for the original precursor, going down to +4, and then reaching +5 again for V_2O_5.

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PS-TuP18 The Increased Efficiency Of The Amorphous/Silicon Heterojunction Solar Cells With Silicon Micro-Channels In Back Side Substrate*, **Hugo Alvarez**, G.L. Bertão, A.R. Silva, F.H. Ciodin, J.A. Diniz,* University of Campinas, Brazil

In this work, silicon based heterojunction (SHJ) solar cells were fabricated without a intrinsic layer using a 200 nm a-Si:H p^+ layer deposited by Electron Cyclotron Resonance-Chemical Vapor Deposition (ECR-CVD) system on to p^+-c-Si substrate. The electrical parameters of the obtained solar cells, such as efficiency, are related to the effects of: i) radio-frequency (RF) chuck power, used during the deposition of amorphous silicon (a-Si:H) Electron Cyclotron ECR-CVD, in the incorporation of H into the a-Si:H films for different RF powers; ii) Silicon micro-channels, which were fabricated in the back-side substrate with the solar cells.

The films were deposited using a ECR power of 500W, pressure of 4mTorr, substrate temperature of 20 °C, gas flows of SiH_4 and Ar, 200 and 20 sccm and 20 minutes and RF power of 1, 3 and 5W. To create the p^+ layer, the samples were boron implanted and annealed in a RTA process. Back and front aluminum contacts of 500 nm were deposited by sputtering and a thin layer of silicon oxide for passivation and an antireflective coating of silicon nitrite was deposited in the ECR for PV Cells efficiency measurements. The back-side contacts were corroded in circular dots (200 µm of diameter) and used as mask to define the silicon micro-channels using ICP (Inductively Coupled Plasma) plasma etching based on SF_6/Ar gas mixture. This SHJ solar cells were fabricated and the current density versus voltage curves in illuminated (AM 1.5) condition were measured. Before the microchannel etching, all solar cells, presented lowest efficiencies of about 0.001%. After the formation of the Micro-Channels (depths of about 7.5 µm and 8.2µm, for 10 and 40 minutes, respectively) using ICP plasma etching increased these values at least one order of magnitude. The maximum of 0.4% of efficiency was obtained for the SHJ cell, which was fabricated with the a-Si:H film of 3W RF power and with micro-channel in back-side, using 10 minutes of ICP etching. In the future, we intend to fabricate a microfluidic system to introduce the fluid into the Micro-Channels to cool and to increase the efficiency values of solar cells.

PS-TuP19 Effect of RF Plasma on H Radical Generation on DCMS Produced a-Si:H*, **Jan Uhlig**, E. Barlaz, D.N. Ruzic,* University of Illinois at Urbana-Champaign

We report on the correlation between hydrogen radical concentrations and the densities of amorphous silicon produced by DCMS in Ar. Previously, the addition of molecular hydrogen during growth at pressures sufficient to produce viable inclusion rates frequently led to blister formation and potential delamination in the final film. An alternative approach demonstrated here is to improve the concentration of hydrogen radicals relative to molecular hydrogen th rough the use of a secondary plasma from an RF coil in the deposition chamber. At 300 W RF power and 1 mTorr of Ar, the addition of a fraction of a mTorr of hydrogen gas leads to a 20% reduction on film density. The relationship between hydrogen radical concentration production and secondary plasma power will be characterized by radical probe measurements.

PS-TuP20 Hardmasks of TiN and Al for Silicon Micro-Channel Definition via ICP Plasma Etching Process*, **Camila Ruiz**,* Plasma Nanotechnology Research Center, UNICAMP, Brazil*; J.A. Diniz, A.M. Rosa,* Plasma Nanotechnology Research Center, University of Campinas, Brazil

TiN and Al films were used as hard mask (HM) materials in Si etching using a high-density inductively coupled plasma (ICP) reactor for silicon micro-channel (SiMC) (with depth > 1 µm) fabrication. The main proposal on this research is define a best hard mask (HM) for silicon micro-channel (SiMC) fabrication using ICP (Inductively Coupled Plasma) etching process. In addition, there are some important properties for hard mask should achieve, such as high mechanical performance and etch resistance to support the high process conditions. The TiN and Al films were deposited on silicon substrate by sputtering. Table 1 presents the obtained samples, with the thickness values and whether the annealing was performed or not.

Table 1. The obtained samples and the Hard Mask (HM) conditions

Samples	HM	Thickness	Annealing
A	TiN	100nm	YES
B	TiN	100nm	NO
C	Al	100nm	YES
D	Al	100nm	NO
E	Al	500nm	YES
F	Al	500nm	NO

Table 2 The used ICP parameters(fixed conditions: P=30mTorr, 450WICP, 100WRIE)

Process	ICP Parameters(sccm)	Time(min)
#1	48SF6+87Ar	10
#2	48SF6+87Ar	20
#3	48SF6+87Ar	30
#4	48SF6+87N2	10
#5	48SF6+87N2	20
#6	48SF6+87N2	30
#7	First sequence:20seconds, 48SF6+87ArSecond sequence:20seconds,48C3F8+87Ar	20
#8	First sequence:20seconds, 48SF6+87N2Second sequence:20seconds,48C3F8+87N2	20

The ICP processes to fabricate the silicon micro-channels (SiMC) and to characterize the mask resistance under the plasma etching were carried out using these fixed parameters as table 2. Two different gas mixtures were used for etching steps without the environment changing: SF_6+Ar, and SF_6+N_2 for 10, 20 and 30 minutes were employed. Two sequences of gas mixtures were used for etching steps in cycles with the gas environment changing: the first cycle was: 20 seconds SF_6+Ar, and in the sequence, 20 seconds, with C_3F_8+Ar; the second cycle was: 20 seconds with SF_6+N_2, and in the sequence, 20 seconds, with 48sccm of C_3F_8+N_2 for 20 minutes. The steps in cycles with different gas environments were based on Bosch process [1,2]. Usually, the Bosch process is performed using the cycles based on one sequence with SF_6/Ar gas mixture, with C_4F_8/Ar. In this work, we have used C_3F_8 gas, instead of traditional C_4F_8. Table 2 shows the conditions of ICP etching processes. The TiN hard masks have presented high resistance to etching process. However, the 100 nm Al films did not present high resistance, because the sputtering mechanism can occur. The 500 nm thick layers (samples E and F, Table 1), have presented the high resistance to etching process.

PS-TuP21 Time- and space-resolved Diagnostics of a Self-Neutralized Ion Beam Extracted from a Pulsed Plasma*, **Ryan Sawadichai**, Y.-M. Chen,* University of Houston*; S. Tian,* Lam Research Corporation*; V.M. Donnelly, P. Ruchhoeft, D.J. Economou,* University of Houston

Ion beams are extensively used in a variety of thin film deposition and etching technologies. To neutralize the space charge of a positive ion beam extracted from a plasma, hot filaments, emitting electrons thermionically, are strategically placed on the downstream side of the extraction grid. Charge neutralization prevents spreading of the ion beam by Coulomb collisions among the ions. This work reports our observation that a self-neutralized ion beam can be obtained when the beam is extracted in the afterglow of a pulsed plasma, in the absence of any hot filaments. Specifically, a nearly monoenergetic ion beam was realized by applying a synchronous DC bias on an electrode in contact with the plasma during a specified time window in the afterglow of a pulsed plasma. Interestingly, the ion beam flux in the pulsed plasma case was much higher than that in a continuous wave plasma, under comparable operating conditions. Time resolved measurements of the ion and electron energy distributions were performed along the beam axis to characterize the spatiotemporal evolution of the beam and arrive at a plausible explanation for self-neutralization. Near the grid, positive ions reach a peak current during the active glow, and again soon after the application of bias in the afterglow, while electron current peaks only at the beginning of the afterglow. At distances greater than 10 cm away from the extraction grid, ions are only detected after the application of bias at a peak current with a delay corresponding to the flight time, while the electron peak did not shift. The time- and spaced-resolved measurements support a mechanism in which electrons from a low-density plasma near the ion extraction grid neutralize the space charge in the transiting beam.

Work supported by the National Science Foundation.

PS-TuP22 Vacuum-ultraviolet-radiation Damage of Low-k Dielectrics*, **J. Leon Shohet**, S.-H. Kim, H.M. Nguyen, P. Xue, J. Blatz, H. Cheng,* University of Wisconsin-Madison*; Y.-H. Lin,* NSRRC, Taiwan*; J.-F. de Marneffe, M. Redzheb, S. Armini,* IMEC, Belgium*; C.-C. Chen,* NSRRC, Taiwan*; Y. Wu,* University of Wisconsin-Madison

VUV exposure of dielectrics during processing can cause damage and can also be beneficial.. The goal of this work is to optimize the "beneficial" spectrum of photon radiation during plasma processing. To fully separate the effects of charged-particle bombardment a synchrotron can be used to provide a continuous spectrum of radiation over the range that most processing plasmas generate. In this work, four low-k samples were provided by IMEC. Their properties before exposure are as follows:

Precursor	Template	UV cure	k value at 100 kHz	
Sample 1	PMO	CTAC (C)	No	2.35
Sample 2	MSQ	BrijL4 (L4)	No	2.36
Sample 3	MSQ	BrijS10 (S10)	No	2.26
Sample 4	MSQ	BrijS10 (S10)	Yes	2.13

To determine the spectral effects of irradiation a five-step procedure was followed. The steps are (1) a rapid photon energy scan to measure the substrate current caused by photoemission as a function of photon energy. (2) Determine which photon energies generate the highest and lowest substrate currents. (3) Irradiate samples separately at the photon energy for the (a) the highest and (b) the lowest substrate current. (4) Measure the substrate current as a function of time for each of the monochromatic irradiations. (5) Following the monochromatic irradiation, a rapid photon energy scan was made again to determine whether changes could be observed in the dielectrics.

For each case, the substrate current begins at a high value and then decays as a function of time until it reaches a steady state. This is typically found after photoemission occurs because the dielectric acquires a net positive charge and thus photoemitted electrons tend to be attracted back to the dielectric. It should be emphasized that the substrate current does not decay to zero but reaches a constant value which is caused by photoinjection of electrons from the silicon substrate.

The damage effects were measured by examining the changes in dielectric constant, dielectric thickness, mechanical properties using nanoindentation, and chemical bond structures using FTIR. It was determined that VUV irradiation with photon energies > 7 eV increased the concentration of silicon dangling bonds in low-k SiCOH. Photons of lower energy were not able to bread the Si-O bonds that have a dissociation energy of 6.3 eV. TDDB degradation and negative mobile-charge generation were observed when the photon energy was greater than 9 eV. The k value increased when the dielectrics were exposed to photon energies > 8 eV. VUV photon irradiation increased the film hardness at photon energies of 10.2 and 11.8 eV. The dielectric constant increased slightly after exposure for all samples.

PS-TuP23 Porous Alumina as a Vacuum Ultraviolet Transmission Window*, **Yuting Wu**, H. Cheng,* University of Wisconsin-Madison*; Y.-H. Lin, C.-C. Chen, H-S. Fung,* NSRRC, Taiwan*; J.L. Shohet,* University of Wisconsin-Madison

Porous alumina is examined as a coupling window between an electron-cyclotron-resonance plasma used as a vacuum ultraviolet vuv source and a separate processing chamber. The porous alumina sample coupon used in this work has the following properties. The sample is 2 x 2 cm. Its thickness is 38 microns. It is composed of pores that are 20 nm in diameter resulting in a porosity of 50%.

To eliminate the effects of particles, a synchrotron was utilized to obtain the transmission properties as a function of photon energy. The transmission of VUV through porous alumina was measured as a function of wavelength is measured and was found to be nearly 50%. A silicon wafer with a dielectric surface is then placed in the processing chamber and exposed to VUV, both with and without the porous alumina window. A Kelvin probe is used to measure the surface charge induced on the wafer by photoemission in both cases, which will determine whether porous alumina can efficiently couple the VUV irradiation to a sample in a processing plasma.without significant modification to its spectrum and its resulting effects on the material. The advantage of porous alumina over a glass capillary-array window is that the hole diameters are in the nanometer range and this minimizes any particle flux compared with the glass capillary array.

PS-TuP25 Development of an In-situ Plasma Enhanced Atomic Layer Etching System for III-group Nitride Device Process*, **C.P. Lin**, Y.H. Lin, C.C. Chen, M.K. Wang,* National Applied Research Laboratories, Taiwan, Republic of Korea*; C.N. Hsiao,* National applied research Laboratories,Taiwan, Republic of Korea*; F.Z. Chen,* National Applied Research Laboratories, Taiwan, Republic of Korea

An in-situ plasma enhanced atomic layer etching system has been design and fabricated. NO_2, BCl_3 and Ar plasma were used as the precursor for AlGaN epitaxy layer at various temperature. The optical detector was used to in-situ monitor the plasma spectrum during the step by step etching process. It is found that the layer by layer etching feature shows the process is a controlled self-limited reaction. In addition, the saturation curve of etching rate and precursor pulsed time has been established. Furthermore, This system could be used for the III-group nitride semiconductor device process.

PS-TuP26 Advances in the Spectroscopic Characterization of Ceramic Films and Coatings*, **Fuhe Li**, A. Tavakoli, J. Brim,* Air Liquide Electronics - Balazs NanoAnalysis

A variety of radio frequency (RF) plasma source atomic optical emission spectroscopy and atomic mass spectrometry have been developed and implemented in our laboratory to characterize various solid ceramic materials, thick coatings and metal-oxide thin films. The techniques that we have developed include but are not limited to glow discharge OES, ICP-OES, laser ablation ICP-MS. Utilizing advanced RF plasma or a high energy laser beam for material sputtering, excitation or ionization, many intrinsic limitations associated with Auger, EDS, GD-MS, RBS, and SIMS techniques such as surface charging are eliminated. The signal intensities produced by these advanced techniques all have a simple and well-defined mathematical (linear) relationship with elemental concentrations in the material. A wide linear dynamic range (over seven orders of magnitude) in these techniques coupled with traceable NIST material standards developed in our laboratory have made accurate surface, interfacial and bulk analyses possible. The advances have also led to a much higher sensitivity in impurity analysis and a much higher accuracy in compositional verification. In addition, deep depth profiling a > 50 µm hard and thick ceramic coating (e.g. Type III anodized coatings) throughout its entire thickness in a real-time fashion can now be accomplished.

PS-TuP27 Effect of Plasma Configuration on Defect-free Functional Doping on Graphene Surface*, **Goo-Hwan Jeong**, S.-I. Jo,* Kangwon National University, Republic of Korea

In this presentation, I will present the effect of plasma configuration on defect-free functional doping on graphene surface. The system is a vertical-type direct-current plasma with parallel electrodes. We change the electrode configuration and adjust the plasma input power and treatment time to utilize various ion-bombardment energies and plasma doses. The up-cathode system with a powered upper electrode and ground lower anode is more suitable than the traditional down-cathode system for efficient plasma doping. This configuration yields a low-energy ion process and thus suppresses high-energy ion-induced damages.

The graphene was prepared by mechanical exfoliation and the doping was performed using ammonia gas. The degree of a structural damage on graphene after the doping was mainly evaluated using Raman spectroscopy. Finally, the structural evolution of graphene and the doping components with respect to the plasma conditions are extensively characterized with Raman spectroscopy, atomic force microscopy, and X-ray photoelectron spectroscopy. In addition, we provide the results of *in-situ* OES analysis during plasma-doping process. The results provide an effective doping condition for doping nanomaterials without plasma-induced damage.

PS-TuP28 Fluid Model Numerical Simulation Analysis of Microwave Plasma Discharges*, **Wan-Ting Chiu,*** National Tsing-Hua University, Taiwan, Taiwan, Republic of China*; I.N. Yeh, K.C. Leou,* National Tsing-Hua University, Taiwan, Republic of China

Microwave plasma discharges have been widely employed for diamond synthesis. In this work, fluid model numerical simulation analysis, using a commercial available code, COMSOL-Multi-physics, has been conducted for microwave hydrogen plasma discharges operated at 2.45 GHz. The simulation model consists of all basic physical mechanisms, including electromagnetics, plasma discharge, gas flow and heat transfer, along with gas phase and surface reactions of gaseous species and charged particles. For our first study, we investigated a plasma reactor based on the TM_{02} mode microwave applicator and a quartz dome. The simulation analysis was first employed to fine tune the structure dimension maximize the coupling of the 2.45 GHz microwave to the desired waveguide mode, TM_{02}, while minimizing its coupling to the major competing mode TM_{01}. The simulation analysis with plasma discharge shows that a plasma ball is formed above the substrate stage for certain operating conditions, while a separate plasma discharge appears if operated outside those operating “window”, a common characteristics of microwave plasma discharge operated under microwave cavity resonator mode. Parametric analysis of plasma discharge characteristics for different gas pressure and microwave power have been carried out. Detailed simulation results will be presented.

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PS-TuP29 Evaluation of Simulation Tool for a Plasma Generation based on the Dual Property of Electrons*, **Shinichiro Kitamoto**, P. Abraha,* Meijo University, Japan

This research presents the development of a simulation tool that characterizes and optimizes the plasma characteristics of a new plasma device based on the dual property of electrons. The plasma device consists of three areas, namely the expansion area, the diffraction area, and the processing area. Successive electrodes generate, expand, and diffract the electrons that dissociate and ionize the nitrogen gas into a plasma. The device is specifically tailored to produce a uniform and large-volume plasma that can harden the surface of large mechanical parts or a large number of mechanical parts. Evaluation of the performance of the plasma device in attaining a uniform and large-volume treated materials requires extensive experimental work, modeling and numerical simulation in addition to plasma diagnostics. In this research, the principle of the plasma generation and the operating conditions of the plasma device are considered in constructing the simulation tool that illustrates the qualitative relations of the plasma parameters against the magnitude and uniformity of the plasma. Numerical simulation of three sequential regions namely particle, wave, and particle regions corresponding to the expansion, diffraction, and processing areas are modeled to give the total framework. The two particle regions, Particle-In-Cell and Monte-Carlo-Collusion methods, are carried out to determine the particle energy and position within the plasma chamber. While in the wave region, the Fresnel theory is used to determine the diffracted electron intensity distribution. In combining the results of the particle and wave regions, the plasma characteristics of the device are holistically determined. Comparison of the results of the simulation and experimental data obtained show good agreement, thus verifying the validity of the simulation tool.

PS-TuP30 Plasma Nitriding of Highly Polished Metallic Surfaces*, **Yoshiki Handa**, P. Abraha,* Meijo University, Japan

This research presents an appropriate plasma nitriding method for highly polished precision metallic components that need to maintain the as-finished surface conditions after the plasma treatment. Conventionally, a nitrided layer consists of a hard but brittle nitrogen compound layer and a layer made of diffused interstitial nitrogen atoms. The compound layers, $Fe_{3-2}N$ (gamma-prime) and Fe_4N (epsilon) form when the phase field has a solubility range of about 6-8 percent weight nitrogen. A high concentration of the nitrogen atoms on the surface, or concentration gradient, drives the atoms along the grain boundaries of the sample to form the diffusion layer. In this research, the incidence of the electrically charged electrons and ions is controlled to suppress the formation of the gamma-prime and epsilon phase fields and maintain a steady flow of interstitial nitrogen atoms along the subsurface. In this configuration, the sample is set inside a shielding grid that is located in the electron beam excited plasma chamber. The shielding grid is a 40-mesh screen biased negatively, while the sample is biased positively. The negatively biased grid repels the electrons that cause overheating in addition to attracting the ions for possible charge exchange with the meshed wire, thus increasing the atom density. On the other hand, the sample is positively biased to avoid any incoming ions from approaching the sample. In this experiment, the driving parameters of the built-in bias configuration were optimized to guarantee a diffusion-based nitriding that suppresses the formation of the compound layer. A comparison is then made based on measurements of the plasma species that interact with the samples and the characteristics of the treated samples in using both the diffusion-based method, neutral nitriding, and the conventional ion nitriding method. The results show neutral nitriding is a successful nitriding method that can strengthen the surface while keeping the surface free of the compound layer.

Reconfigurable Materials and Devices for Neuromorphic Computing Focus Topic
Room Hall B - Session RM-TuP

Reconfigurable Materials and Devices for Neuromorphic Computing Poster Session

RM-TuP1 Selector-less Crossbar Array through Self-rectifying Characteristic of Pt/HfO₂/Ti Memristor*, **Yong Kim**, S.Y. Ryu, W.H. Jeong,* Seoul National University of Science and Technology, Republic of Korea*; K.-S. Min,* Kookmin University, Republic of Korea*; B.J. Choi,* Seoul National University of Science and Technology, Republic of Korea

DRAM and flash memory currently being used as working memory devices must be configured with transistors. For this reason, it has been reached the limits of scaling, power consumption and fabrication cost. In order to overcome these limits, next-generation memory devices have been developed and materials/device structures have been studied actively. Memristor could be used as a nonvolatile memory with simple crossbar array (CBA) structure. Although CBA structure is possible to innovatively overcome the scaling limits, it has major problem, so called sneak path current. It is caused by cross talking near the selected cell and typically solved by adding an additional selector device (e.g., diode, transistor, etc.). Recently, self-rectifying memristor could be enabled by bilayer stack, which could much simplifying the CBA structure: selector-less CBA. We fabricated the 10x10 and 30x30 CBA as selector-less memristor device using the potential barrier between each stack of the fabricated MIM structure.

In this study, we have acquired the self-rectifying characteristics for CBA structure using the $Pt/HfO_2/Ti$ device. The device was fabricated 10x10 and 30x30 CBA patterned with 2 – 20 µm of electrode size. The top/bottom electrodes were deposited using electron beam evaporator and the dielectric material was deposited by atomic layer deposition (ALD). HfO_2 layer grown by ALD plays the role of switching layer in memristor. The thickness of the switching layer was quite thin, which eliminates the need for electroforming process. In addition, we obtained the self-rectifying characteristic that does not permit the fluent current conduction under negative bias through the potential barrier between Pt and HfO_2 layer.

As a result of electrical properties, this device follows an interface-type switching mechanism in which the current value decreased as the electrode size decreased. By inserting Al_2O_3 layer of 1 - 2nm, it was confirmed that switching occurs in HfO_2/Ti interface. The size of the formed conductive region was changed through the positive bias and the stability of the rectifying function was verified by applying the negative bias up to -

3V. We confirmed the uniformity of memristor cells randomly chosen among 10x10 and 30x30 CBA and verified the device-to-device variability. Cycle-to-cycle variability was also obtained from these cells through a switching of more than 100 cycles. Finally, the AC measurement was applied to explore the possibility of fabricated device as a synaptic device.

RM-TuP2 Electron Beam Induced Current Microscopy of Interfacial Barrier Effects in Al_2O_3/TiO_x Resistive Switches*, **Brian Hoskins,*** National Institute of Standards and Technology (NIST)*; G. Adam,* National Institute for R&D in Microtechnologies (IMT Bucharest), Romania*; E. Strelcov,* National Institute of Standards and Technology (NIST)/University of Maryland*; A. Kolmakov, N.B. Zhitenev,* National Institute of Standards and Technology (NIST)*; D. Strukov,* University of California at Santa Barbara*; J. McClelland,* National Institute of Standards and Technology (NIST)

Resistive switching devices (ReRAM) represent a broad class of two-terminal continuously tunable resistors including memristors, phase change memory (PCM), valence change memory (VCM), and electrochemical metallization cells (ECM). Though these devices, especially PCM, are increasingly being commercialized by industry for use in next generation memories, they are also all actively studied for use as synaptic weights in next generation hardware-accelerated neuromorphic networks.

We have previously investigated Electron Beam Induced Current Microscopy as a means of reliably characterizing resistive switches. In that investigation, we observed surprising electronic effects, such as internal secondary electron emission, in addition to more traditional electron-hole pair separation, and we broke those up into constituent currents based on their origin through Monte-Carlo modeling of the electron beam-matter interaction.

Now, armed with a new understanding of the physics of EBIC imaging, we study the impact of manufacturing variations on resistive switches by continuously tuning the thickness of an Al_2O_3 interfacial barrier. Shifts in the apparent ratios of internal secondary electron emission from the top electrode to the bottom electrode and vice versa appear to indicate a continuous tuning of the apparent filament diameter as both a function of the injected current and the interfacial barrier thickness. This yields an apparent reduction in the current density, the primary effect of which is a reduction in the device damage from forming and a suppression of parasitic leakage currents imaged in devices without interfacial barriers.

Advanced Surface Engineering Division
Room Hall B - Session SE-TuP

Advanced Surface Engineering Division Poster Session

SE-TuP2 Fabrication of Porous Membranes of Controlled Porosity and Chemical Functionality*, **Golnaz Dianat**, M. Gupta, S. Seidel, M.M. Deluna,* University of Southern California

We present a modified initiated chemical vapor deposition (iCVD) technique to synthesize porous polymer membranes. We demonstrate that we can pattern the deposition of the porous polymer membranes by using poly(dimethylsiloxane) (PDMS) masks. The porosity and thickness of the membranes can be controlled by varying the substrate temperature during monomer deposition. The functionality of membrane can be tuned by addition of a cross-linker during polymerization and allow for the fabrication of robust free-standing shaped membranes. Our ability to control the shape, thickness, porosity, and functionality of the porous membranes allows for the design of new surfaces for a variety of applications in sensors, filtration, and microfluidics. Asymmetric polymer membranes, that are composed of a dense top layer and porous bottom layer, can be synthesized using a combination of conventional and nonconventional iCVD conditions in a one-pot process. This method allows for a high degree of control over the thickness of the dense layer by simply controlling the deposition time and paves the way to synthesize ultrathin dense layers with sub-50nm thickness that is difficult to attain using other methods. The functionality of the dense and porous layers can be independently tailored to be either hydrophobic or hydrophilic, resulting in membranes that are fully hydrophilic, fully hydrophobic, or asymmetric in both structure and chemical functionality.

SE-TuP3 Plasma Treatment of Thiol-Carborane Self-Assembled Monolayers on Copper*, **Michelle Paquette**, R. Thapa, L. Dorsett, S. Malik, S. Wagner, A.N. Caruso,* University of Missouri-Kansas City*; D. Merrill, J.D. Bielefeld, S.W. King,* Intel Corporation

Thiol-carborane self-assembled monolayers (SAMs) have been used to modify the properties of metal surfaces. Not only do the symmetric twelve-vertex icosahedral carborane molecules provide a unique and appealing geometry for SAM formation, but boron carbide materials are notorious for their chemical, thermal, and mechanical robustness. Carborane-based SAMs have been shown to provide superior corrosion resistance on silver as well as the ability to modify the electronic properties (e.g., work function) of gold and silver surfaces. One of the noteworthy properties of carboranes is their ability to cross-link via labile hydrogen bonds under the influence of heat, plasma, and various energetic particles. Here, we investigate the influence of various plasma treatments on carborane monolayers on copper and show how these can be used to both further tune their properties as well as influence their stability.

SE-TuP4 Improved Light Extraction Efficiency using Homeotropic Thin Films on SiO_2 Micro Pillars*, **J.H. Lee**, Y. Lin, G. Wu,* Chang Gung University, Taiwan

It has been known that high refractive index material such as gallium nitride film has been limited for light extraction by low total internal reflection angle. The external quantum efficiency for a light-emitting diode is thus low due to absorption by the semiconductor material and the substrate. In this paper, we proposed to use homeotropic, vertical alignment, liquid crystal polymer coatings on patterned SiO_2 micro - pillar arrays to improve the light extraction of nitride light-emitting diodes . A wet etching technique was firstly employed to create the patterned SiO_2 micro-pillar arrays on the surface. The pillar was nominally 3 µm in diameter, 200-600 nm in height, and the period was 6 µm for a triangular array. Then we coated 5 wt% liquid crystal polymer precursor uniformly on the surface of the etched structure. The results showed that the homeotropic optical thin-film improved light guiding, and the light escape cone angle increased from 26 to 50-60 degrees by the viewing angle test system at an injection current of 20 mA. The light extraction efficiency was also increased by 59% by using an integrating sphere.

Keywords: Liquid crystal polymer, Light-emitting diode, SiO_2 micro - pillar

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SE-TuP5 Investigating the Influence of Substrate Cleaning on the Solution Stability of Plasma Polymer Films*, **Karyn Jarvis**,* Swinburne University of Technology, Australia*; S.L. McArthur,* Swinburne University of Technology and CSIRO, Australia

Plasma polymerization modifies surfaces via the deposition of a thin film possessing specific functional groups. The organic monomer is introduced into the low pressure chamber as a vapour, fragmented via radio frequency and deposited onto all surfaces in contact with the plasma. Commonly used monomers such as octadiene, allylamine and acrylic acid enable the deposition of hydrocarbon, amine and carboxylic acid terminated surfaces respectively. Surface cleaning prior to the deposition of thin films is frequently carried out to improve film adhesion. The use of plasma polymer films in biomedical applications has increased the demand for coatings suitable for use in physiological conditions. Significant changes in film properties in aqueous conditions have serious implications on the incorporation of these films in biomedical technologies and devices.

In this study, silicon wafer substrates were cleaned by several different methods prior to the deposition of plasma polymerized thin films to investigate the influence of substrate cleaning on film stability in aqueous solutions. The substrates were used untreated or cleaned by liquid sonication, UV/ozone cleaning or air plasma. X-ray photoelectron spectroscopy (XPS) and contact angle measurements were undertaken to determine the effect of the cleaning method on surface chemistry and wettability. After cleaning, the substrates were coated by plasma polymerized octadience, acrylic acid or allylamine thin films. The surface chemistries and film thicknesses of the plasma polymerised films were determined by XPS and variable angle spectroscopy ellipsometry respectively. The plasma polymerised films were immersed in both Milli-Q water and phosphate buffered saline for time periods of 1, 24 and 168 hours. Films were again analysed via XPS and ellipsometry to determine the influence of substrate cleaning, immersion solution and immersion duration on film stability. Substrate cleaning was shown to have an influence on film stability with visible pitting on some films, even after only 1 hour of immersion. Substrate cleaning is an important step prior to the deposition of thin films and can be used to extend the solution stability of plasma polymerised films, which has important implications for a variety of biomedical applications.

SE-TuP6 Tribological Systems Solutions for Gas Turbine Engines*, Pantcho **Stoyanov**,* Pratt & Whitney

The advancement of durable gas turbine engine components depends heavily on the development of high-performance materials, which can withstand extreme environmental and contact conditions (e.g. large temperature ranges, high contact pressures, and continuous bombardment of abrasive particles, all of which degrade the physical properties). In particular, due to the large number of complex contacting and moving mechanical assemblies in the engine, the lifetime of certain structures is limited by the tribological performance of the employed materials and coatings. This talk will provide an overview of tribological solutions employed in several sections of gas turbine engines. After a general review of aircraft engine tribology, the talk will focus on coatings used for clearance control (i.e. abradable air seals) as well as tribological materials used to minimize fretting type of wear. More specifically, a study will be presented on the influence of self-lubricating hexagonal boron nitride (hBN) on the erosion and abradability of Ni-based abradable coatings. Subsequently, a series of studies on the friction and wear behavior of Ni-based and Co-based superalloys at elevated temperatures will be presented. Emphasis will be placed on the correlation between the third body formation process (e.g. oxide layer formation, transferfilms) and the tribological behavior of the superalloys. This talk will conclude with the future strategies of tribological coating solutions in Pratt & Whitney's PurePower® PW1000G family of engines.

SE-TuP7 Effect of Laser Processing on the Atmospheric Corrosion Behavior of Mg Alloy AZ31B and Weldments*, M.A. Melia,* Sandia National Laboratories*; L. Agnew, J.M. Skelton, J.R. Scully, **James Fitz-Gerald**,* University of Virginia

The widespread implementation of lightweight magnesium alloys to the automotive and aerospace industries is currently limited by its poor and unpredictable corrosion response. Of major concern is the localized corrosion of Mg alloys, driven by a uniform population of electrochemically noble secondary phases present in the chemically heterogeneous microstructure, resulting in a rapid loss of structural integrity. These microstructural heterogeneities are accentuated when Mg alloys are welded causing galvanic coupling between weld zones. A research investigation to mitigate localized corrosion of a Mg alloy (AZ31B), with and without weldments, via laser surface engineering has been conducted. Lasers operating in a nanosecond pulse duration regime are capable of melting and solidification rates on the order of 10^9 K/s with the ability to extend the solid solubility limit of the alloying elements. The irradiation of AZ31B with an excimer laser (FWHM= 25ns, λ= 248nm) observed significant changes in the near surface microstructure and secondary phase particle dissolution, characterized in this case by scanning electron microscopy equipped with a backscatter electron detector. The corrosion response of Mg alloy AZ31B (3wt% Al, 1wt% Zn, 0.6wt% Mn, and Mg balance) was investigated using the accelerated atmospheric test (GMW14872) for 30 wet-dry cycles. The atmospheric exposure test consists of a 24-hour cycle involving three 8-hour stages. During the first stage, samples are held at ambient temperature and humidity (25 °C, 45% RH) and are sprayed every 90 minutes with a salt solution (0.9% NaCl, 0.1% $CaCl_2$, 0.075% $NaHCO_3$). During the second stage the temperature is increased to 49 °C and samples are continuously sprayed with a deionized water fog (~100% RH). During the third stage temperature is increased to 60 °C and held at less than 30% relative humidity. The corrosion product was analyzed using Fourier transform infrared spectroscopy (FTIR) and grazing incident x-ray diffraction (GI-XRD). At early stages of the exposure experiments the laser processed specimens showed less corrosion product coverage than as-polished or welded specimens.

Surface Science Division
Room Hall B - Session SS-TuP
Surface Science Division Poster Session

SS-TuP1 Encapsulation of Metallic Nanoparticles near the Surface of Graphite*, **Ann Lii-Rosales**[1,2], P.A. Thiel,* Iowa State University and Ames Laboratory

Graphite, in the bulk, is known to form graphite intercalation compounds (GICs) with certain elemental metals, for example, rare earths, alkali metals, and alkaline earths. These metals can insert between graphene sheets and alter the magnetic or transport properties of graphite. While intercalation in the bulk of graphite has received much attention, considerably less has been paid to intercalation near the *surface* of graphite, underneath only one (or a few) graphene layers. First of all, can one trap metals just beneath the graphite surface? Do the surface-intercalated metals adopt different structures compared to their bulk counterparts? What is the driving force for such surface intercalation? These questions motivate our work.

The presentation will encompass strategies for achieving *surface* intercalation of metals in graphite. In short, we find that trapping metal atoms just beneath the graphite surface requires two specific conditions: (1) ion-induced defects on the graphite surface, and (2) elevated temperature during metal deposition. We find that this strategy works for a variety of metals, and the growth temperature is metal-specific. Results on dysprosium, copper and ruthenium will be presented. We use scanning tunneling microscopy to probe and characterize the surface intercalation. Based on experimental results and density functional theory, we find that the intercalated metal atoms at the graphite surface adopt *much different* structures compared to those in bulk GICs – "encapsulated" may be a better descriptor than "intercalated". Furthermore, metals that are not known to form bulk GICs *can* be encapsulated at the graphite surface. Finally, we find that some of the metals are well protected from atmospheric oxidation by the graphene overlayer. Our synthetic strategy opens up a new avenue for metals to interact with the graphite surface, and to create novel surface nano-structures.

SS-TuP2 Uncovering the Mechanism of Thermal Dry Etching of Cobalt Thin Films Using Hexafluoroacetylacetone (hfacH)*, **Mahsa Konh**, J. Zhao, A.V. Teplyakov,* University of Delaware

The initial steps of thermal dry etching of cobalt thin films with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone, hfacH) as the organic precursor were studied with in situ temperature-programmed desorption (TPD) and with X-ray photoelectron spectroscopy (XPS) supplemented with microscopic investigations. Comparison of the reaction of hfacH with oxidized and clean (sputtered) cobalt thin films suggested that partial surface oxidation is essential in designing dry etching schemes of this metal. On a clean surface, decomposition of the organic precursor molecule was the primary surface process. The oxidized cobalt surface can be reduced by a reaction with hfacH, releasing $Co(hfac)_2$ and water (as a side product). However, the thermal chemistry occurred at temperatures significantly higher than those required for industrial applications. The kinetic contribution to the overall etching process was investigated by exposing the oxidized cobalt films to hfacH at several temperatures and following the chemical and morphological changes of a surface. It was determined that exposure to hfacH affected the nanostructuring of the surface even at room temperature (making the surface rougher). Annealing this surface to 800 K produced a much smoother film following $Co(hfac)_2$ and water removal; however, at that point the films also started to produce microscopic level defects (pits). The optimization of surface temperature placed the upper limit of the process, before substantial surface decomposition of the hfacH precursor molecule and significant morphological changes took place, at 650 K. Further studies are required to explain the experimentally observed possibility of cobalt surface etching at temperatures as low as 440 K.

SS-TuP3 Revealing the Atomic Scale Insights for CO_2 Dissociation on the Rh(111) Surfaces at Ambient Pressure*, **Won Hui Doh**,* Institute for Basic Science (IBS), Republic of Korea*; J. Kim,* Institute for Basic Science (IBS), Republic of Korea*; J.Y. Park,* Institute for Basic Science (IBS), Republic of Korea

Carbon dioxide (CO_2) in the atmosphere is one of the main cause of the greenhouse effect due to CO_2 molecules absorb the infrared radiation

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

[2] **National Student Award Finalist**

emitted by the Earth's surface. Since the Industrial Revolution in 1750's, the concentration of CO_2 in the atmosphere is continuously increased owing to increase of its emission in the economic sector such as electricity and heat production, industry, transport, and etc. Therefore, the utilization of CO_2 has received great attention from many researchers because of the challenging issue to use CO_2 as an energy resource.

A fully oxidized form of carbon e.g. CO_2, however, is a very stable compound which has two double bonds between carbon (C) and oxygen (O) in opposite direction. To facilitate the CO_2 utilization, as the first step of the reaction, the bond between C and O need to weaken or broken for further reactions. Rhodium is well known reducing material which can offer its electrons to the reactants. Previous research on CO_2 reduction reaction showing that CO_2 molecules have a bent structure or CO_3^{2-} after they adsorbed on a catalyst surface by using vibrational and spectroscopies such as IRARS and XPS. However, there is no direct observation for the bent structure of CO_2 on the catalyst surface. Here, we will show the first atomic-scale observation of bent CO_2 adsorption on Rh(111) surface as an intermediate by using near ambient pressure scanning tunneling microscope (NAP-STM). Furthermore, we will discuss the possible mechanism of CO_2 dissociation on Rh(111) based on the NAP-STM images of CO and O_2 adsorption structures on Rh(111) at NAP conditions.

SS-TuP4 Study of Spin Dependent Electrochemical Charge Transfer Across the Ferromagnetic Electrode/Solution Interface*, **Mika Tamski**, F. Blumenschein, C. Roussel, J.-P. Ansermet,* Ecole Polytechnique Fédérale de Lausanne, Switzerland

The Pauli Exclusion principle is known to result in spin dependent charge transfer, where the current is rectified for spins of the same orientation compared to the spins of opposite orientation.[1,2]

Similar spin selectivity has been observed for Ferromagnetic electrodes such as Nickel and Cobalt in electrochemical systems, where chiral molecules have been used as spin filters for selecting one spin orientation over the other. [3,4]

Here we report the progress concerning our studies of spin dependent charge transfer across a ferromagnetic-electrode/solution interface, using the following methodology (Fig.1, online at organiser's website):

1. Saturating the magnetization of the electrode and polarising the spins of radicals in the solution phase by applying a magnetic field B_0.

2. Applying a negative potential to the electrode to induce a charge transfer from the electrode to the paramagnetic species in the solution.

3. Introducing spin-flips of the radical spins with resonant microwave irradiation B_1.

4. Detecting the modulation of the reduction current as a function of modulation of the B_0 or B_1 amplitude, i.e. an electrically detected magnetic resonance (EDMR) experiment.

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SS-TuP5 Two-faced Steps: How Molecular Alignment does and does not Impacts O_2 Sticking Dynamics on Pt.*, K. Cao,* Leiden University, Nederland*; M. Kurahashi,* National Institute for Materials Science, Japan*; **Ludo Juurlink**,* Leiden University, Nederland

Adsorption and dissociation of O_2 on Pt are intensely studied reactions. In heterogeneous catalysis, it is claimed to be of high importance to automotive air pollution control. In electrochemistry, the oxygen reduction reaction limits the efficiency of hydrogen fuel cells. From previous dynamical and spectroscopic studies, it is well-established that O_2 does not dissociate as an elementary reaction on Pt(111). It requires trapping in a chemisorbed molecular state prior to dissociating. Surface corrugation enhances the sticking probability for O_2 at low incident energy, whereas at higher incident energy the influence depends on the step type causing corrugation. In this contribution, we study the origins of these findings combining two recently developed techniques. First, we apply a curved single crystal approach in combination with supersonic molecular beam techniques with high spatial resolution. At low incident energy, the enhanced reactivity is linear with step density and nearly identical for two different step types over a step density range covering approximately two orders of magnitude. At high incident energy, the enhancement mostly disappears. These result suggest energy-dependent dominance of parallel mechanisms causing sticking and dissociation. Second, we use spin-rotation state-selected and aligned O_2 to determined how rotation parallel and perpendicular to the (111) plane and the step direction affect dissociation on 'flat' Pt(533), Pt(553) and Pt(111) single crystals. At lower incident energy, activated molecular chemisorption on the (111) plane strongly favors helicoptering O_2 molecules. This effect diminishes with increasing kinetic energy. The A- and B-stepped surfaces show, on the contrary, at low incident energy no dependence on the orientation of the molecular axis upon impact. This is ascribed to the dominance of initial scattering into a physisorbed state preceding molecular chemisorption and dissociation. At higher incident energy, this mechanism loses its dominance and steps become stereodynamically selective. We observe a clear preference for O_2 molecules impacting with the molecular axis parallel to the step facet.

SS-TuP7 Crystallinity-Transport Investigations of Nanoscale Ru Conductors at Al_2O_3 and/or SiO_2 Interfaces*, **Asim Khaniya**, S. Ezzat, W.E. Kaden, K.R. Coffey,* University of Central Florida

Enhanced scattering of charge-carriers at sufficiently small dimensions[1] (on the order of the mean free path of electrons), also known as the resistivity size-effect, leads to non-scalable increases in resistivity in conductors. As the trend of miniaturization continues in microelectronic fabrication, this size effect becomes a major challenge to current CMOS technology (Cu based) due to the loss of the majority of power at the interconnects due to their larger abundance. By using single-crystalline sub-nanometer metallic interconnects, room temperature ballistic conduction may be achieved. Within this general area of research, Ru has emerged as a promising candidate to replace Cu due to its weaker resistivity-thickness interdependence.[2] In practical applications, interconnects are necessarily in contact with isolating dielectric materials, and this work includes studies of Ru (0001) films epitaxially grown on c-axis sapphire, both with and without various silica capping layers in various states of crystallinity and chemical interaction with the underlying metal. The overall goal of the project is to measure the transport properties of the controllably different samples, while providing sufficient materials characterization to unequivocally establish correlations between changes in resistivity and changes in bulk/interface conductor properties.

To-date, efforts within our group have centered on physical characterization of films produced by collaborators from the Coffey Group in MSE at UCF, and early-stage efforts at reproduction of established SiO_2 thin-films via physical vapor deposition (PVD) within UHV. X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) have been used to demonstrate a high degree of both surface cleanliness and long-range crystal order following large-scale growth recipes carried out by the Coffey group. Further investigation has shown clear correlation between the extent of Ru oxidation and sheet resistivity following different annealing procedures during the film growth recipes. XPS, LEED, and low energy He^+ ion scattering spectroscopy (ISS) have been used to characterize our in situ SiO_2 film growth, which is highly dependent upon both coverage and oxidative crystallization temperature. Further, in-situ measurement of resistivity of Ru(0001) and SiO_2/Ru(0001) films will be made and additional atomically localized information will be collected using scanning tunneling microscopy (STM).

SS-TuP8 Iron Oxide Surface Transformations Revealed by AP-XPS for Ammonia Synthesis*, **Mikhail Trought**,* Michigan Technological University*; E.J. Crumlin, S. Nemsak,* Advanced Light Source, Lawrence Berkeley National Laboratory*; K.A. Perrine,* Michigan Technological University

The industrial synthesis of ammonia, known as the Haber-Bosch process[1, 2], occurs at high temperatures and pressures where hydrogen (H_2) and nitrogen (N_2) react to produce ammonia (NH_3). The dissociation of nitrogen is known as the rate-limiting step on the surface of an iron oxide catalyst.[3-6] At equilibrium conditions, this reaction is well-known, however the surface transformations of the iron oxide single crystal surfaces have not been explored in the near-ambient pressure (intermediate) regime, which may allow for a better understanding of the role of the surface sites and transformations under pressure regimes between traditional surface science (in ultra-high vacuum) and reaction conditions (high pressures).

Synchrotron radiation ambient pressure-X-ray photoelectron spectroscopy (AP-XPS) was used to measure changes in the surface structure and oxidation states of single crystal Fe_3O_4(001) (magnetite) and α-Fe_2O_3(0001) (hematite) surfaces near-ambient pressure conditions. Adsorption of N_2,

H_2, and O_2 on single crystal Fe_3O_4(001) and α-Fe_2O_3(0001) surfaces was measured as a function of temperature and pressure to gain a better understanding of the fundamental surface reactions associated with ammonia formation. In particular, the shape and states in the valence band photoemission spectra were examined to measure the affect of oxidation and reduction of the surfaces.[7] The valence band region helped to identify the states associated with the Fe^{2+} and Fe^{3+} cations in each compound highlighting the differences in structure between magnetite, hematite and the transformations that occurred due to the oxidative and reductive environments. The states present in the N1s, Fe2p and O1s regions complemented the changes in the valence band region observed on the iron oxide surfaces. The results reveal N_2 adsorbs on Fe_3O_4(001) but not α-Fe_2O_3(0001). These studies give insight into the complexity of adsorption processes and surface transformations during heterogeneous catalysis that merge surface science experiments with reaction conditions.

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SS-TuP9 Surface Energies of Thin Oxides of Si(100) as Function of Thickness, Composition and Surface Processing

Saaketh Narayan*, J.M. Day, N. Herbots, A. Brimhall, A. Mascareno,* Arizona State University*; A. Krishnan,* Harvard University*; S.D. Whaley,* Arizona State University*; R.B. Bennett-Kennett,* Stanford University*; K.L. Kavanagh,* Simon Fraser University, Canada

Processing modifies hydroaffinity, reactivity, and total surface energy, γ^T, of semiconductor oxides. Si(100) and its oxides are studied, including native oxides, conventional thermal SiO_2, Rapid Thermal Oxides (RTO), Rapid Thermal Annealed (RTA) oxides, RCA processed Si, Herbots-Atluri (HA) passivated [1] Si, alpha-quartz SiO_2, and oxides after HF-based etching. Correlating surface energies of Si(100) and SiO_2 to composition and processing can reproducibly establish the metrology needed for wafer bonding. Cross-bonding is key in bonding conducted at T < 220°C, or NanoBonding™, [2,3] for Si(100) to SiO_2, GaAs(100), and $LiTaO_3$. Si(100) and Si(111) samples investigated include B-doped p- and p+ wafers, and P-doped n- and n+ wafers.

The surface energy of 50 wafers is measured via Three Liquid Contact Angle Analysis (3LCAA) using the van Oss-Chaudhury-Good (vOCG) model for semiconductors and insulators. The γ^T includes Lifshitz-van der Waals interaction, γ^{LW}, interaction with electron donors, γ^+, and with acceptors, γ^-. Reproducibility of contact angle measurements to extract γ^T, γ^{LW}, γ^+, and γ^- is achieved by metering µL droplets of 18 MΩ deionized H_2O, glycerin, and α-bromonaphthalene in a class 100/ISO 4 laminar flow hood. 4 contact angles are extracted from each droplet and its reflection through 18 MP images analyzed automatically via the Drop and Reflection Operative Program (DROP) which removes subjectivity and speeds up analysis. 30 droplets yield 120 angles, with an accuracy of 3%.

MeV Ion Beam Analysis (IBA) combining <111> channeling with nuclear resonance yields ^{16}O coverage, which is then correlated to γ^T, γ^{LW}, γ^+, and γ^-. Native oxides on p- Si are always hydrophilic, with a γ^T of 53 ± 2 mJ/m^2. RCA wafers have a lower γ^T of 47.3 ± 0.5 mJ/m^2, as RCA removes impurities, but are still relatively hydrophilic. Next, RTA oxides exhibit a lower γ^T than RCA oxides, as thicker oxides are more hydrophobic, corroborated by higher ^{16}O coverage. H-A wafers have a lower ^{16}O coverage but also a more hydrophobic γ^T of 37.3 ± 1 mJ/m^2, being terminated with ordered $Si_2O_4H_4$. RTO on H-A wafers yields the most hydrophobic surfaces with γ^T = 34.5 ± 0.5 mJ/m^2. IBA on native oxides of p- Si detects 13.3 ± 0.3 ^{16}O ML, while IBA on H-A and HF etched Si detects 11.8 ± 0.4 ^{16}O ML. IBA on RTA and RTO oxides show that thicker oxides yield more hydrophobic surfaces. In summary, 3LCAA in conjunction with IBA yields new insights in the relationship between γ^T, oxygen coverage, and processing.

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SS-TuP10 Space Weathering Effects at the Surface of Thin-Film Aluminosilicate Model Regolith

Bijoya Dhar*, W.E. Kaden,* University of Central Florida

Space weathering effects on volatile-rich airless bodies have been studied far less extensively, than those anhydrous interfaces. Although the presence of volatile resources has been established by recent space exploration missions, the fundamental physics and chemistry behind volatile formation and sequestration, associated with radiation processing of regolith, is yet to be thoroughly explored. Therefore a systematic and integrated study of the effect of radiation processes on regolith is needed to better understand the fundamental driving forces governing the volatile transformation at the interface of such bodies. Accordingly, the overall goal of the project is an in situ study of regolith, irradiated with laboratory-based sources within a UHV system, mimicking solar wind processes on airless bodies in space.

To carry out this work, our group is leveraging established thin-film recipes to generate and characterize a well-ordered regolith simulant within our multi-purpose UHV system. Herein we use aluminosilicate ($Al_xSi_yO_z$) sheets as model regolith. The $Al_xSi_yO_z$ film will be grown on a ruthenium (Ru) substrate via sequential PVD of Al and Si in the presence on O_2. The Ru is cleaned with repeated Ar^+-sputtering/annealing. XPS and He^+ ISS have been used for cleaned Ru to ensure surface cleanliness (no detectable contaminants) and LEED for long-range crystal order (sharp 1x1 hexagonal pattern). Initial silica (SiO_2) thin-film growth has been employed to establish both coverage and oxidative crystallization temperature. Using the calibrated Si flux and relative XPS sensitivity factors, Al flux will be calibrated, and both will be used to create bilayer $Al_xSi_yO_z$ film. In addition to the XPS, ISS and LEED, atomic scale confirmation of planar/crystalline silicate layers will be provided by STM analysis.

To simulate solar wind processing of model regolith, we will use irradiation facilities available in our lab, such as an electron gun, an ion gun, and an X-ray source. The physical and chemical characterization of radiation-induced defects to the fabricated $Al_xSi_yO_z$ sheet (like those previously reported by others for SiO_2 film) will be investigated with the in-house equipment. Previously established experiments used to investigate SiO_2 will be helpful to study the electron-stimulated desorption of volatiles. In addition, $Al_xSi_yO_z$ film transference to other supports will be attempted in support of collaborative efforts with others.

Our methods encompass surface science methodologies for radiation investigation on regolith samples, which will help to minimize the gaps in knowledge related to space weathering effects on the airless bodies.

SS-TuP11 Identification of Surface Processes in Individual Minerals of a Complex Ore through the Analysis of Polished Sections using Polarization Microscopy and X-ray Photoelectron Spectroscopy (XPS)

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The changes at the surface level of a mineral during ore processing is of fundamental

importance for the improvement of strategies aimed at increasing the efficiency of metal

extraction. This task is often difficult due to the refractory behavior of minerals and the

deficiency of valuable metals within them. Specifically, surface processes such as metal

readsorption (preg-robbing) on specific minerals are difficult to evaluate, this process can block

or encapsulate the valuable mineral and affect negatively the extraction process. In this study,

we show a powerful approach, through which surface processes in individual minerals are

identified by combining polarization microscopy (MP) and X-ray photoelectron spectroscopy

(XPS). A silver-containing polymetallic sulfide ore from the Peruvian central Andes (pyrite-based with small amounts of galena and covellite) is evaluated, and we track the gradual changes in the sample during the course of leaching with cyanide. The polarization microscopy technique identifies mineralogical species such as pyrite, galena, and covellite, while XPS provides evidence of readsorption of lead on the surfaces of pyrite and covellite after leaching, possibly as lead oxide or thiosulfate. The surface of pyrite does not show significant changes after leaching process according to the microscopic result, although species of oxidized iron are detected together with the readsorption of lead by XPS. The methodology shown here is a tool of significant importance for understanding complex surface processes affecting various minerals during metal extraction and highlights the importance of using surface analytical techniques for the development of novel strategies in the mining industry.

SS-TuP12 Effect of Surface Roughness, Etch Pits, and Adsorbates on the Surface Phonon Density of States of Graphite*, Krishnan Swaminathan-Gopalan*, *K. Stephani,* University of Illinois at Urbana-Champaign

Gas-surface interactions are encountered in a wide variety of disciplines and a detailed understanding of the underlying physics is critical. When a gas-phase particle strikes a surface, it can undergo adsorption, direct impact reactions, or inelastic scattering. These processes are coupled with the phonon bath at the material interface. During the interaction, energy transfer occurs both between and within the sub-systems (substrate and gas particle). A number of mechanisms including multi-phonon processes, translational and internal mode excitations may be captured by the evaluation of the detailed scattering kernels and transition matrix of the gas-phonon interaction. Such a framework provides a powerful alternative to full molecular dynamics (MD) for computing various surface interaction quantities such as accommodation coefficients, adsorption and reaction probabilities, etc. Further, since this framework captures the underlying microscopic details, and can be extended to describe the system in the state of extreme non-equilibrium. These theoretical models have been shown to provide excellent agreement with experiments.

In this work, we will focus on understanding the effect of (i) random surface roughness, (ii) etch pits, and (iii) adsorbates on the phonon density of states of carbon using Molecular dynamics (MD). The phonons at the surface are qualitatively and quantitatively different from the bulk due to the broken symmetry. In addition, the roughness of engineering material surfaces affects the phonon distributions. Furthermore, the gas-surface interactions also alter the PDOS due to the presence of adsorbates on the surface and removal of surface atoms due to surface participation reactions. This results in a highly coupled and dynamic system. Random surface roughness in MD will be obtained via irradiation with low energy particles. The effect of varying height and density of the defective region on the PDOS of this system will be investigated. The etch pits produced as a result of removal of surface atoms resembles a semi-ellipsoid with larger diameters and shorter depth. Here, the phonon distribution will be characterized as a function of both diameter and depth of the etch pits. Finally, the effect of adsorbates on the PDOS will be studied in terms of bond strength (physisorbed vs chemisorbed) and surface coverage.

SS-TuP13 Variation of Structure Colors of Copper with LIPSS(Laser-Induced Periodic Surface Structure) by Femtosecond Laser Irradiation*, TaeHoon Park*, *J.H. Kim, T.Y. Hwang, J.J. Kang,* Korea Institute of Industrial Technology (KITECH), Republic of Korea*; K.B. Kim,* Sejong University, Republic of Korea*; H.S. Lee,* Korea Institute of Industrial Technology (KITECH), Republic of Korea

The Laser-Induced Periodic Surface Structure (LIPSS) formed under femtosecond laser irradiation has been a way to change optical, tactile, hydrophobic properties, etc. without chemical reaction. Specially, the LIPSS can be applied to enhance the visual perception of skin materials in order to meet the user's aesthetic choice of mobiles, auto vehicles, electronics, etc. It has been reported through many studies that the structure color by LIPPS is due to the refraction of the light by periodically nano-scaled structure, however, its variation of structure colors has not been studied generally on the microstructures such as pitch and depth of nano-scaled microstructure. In this study, the metal substrates consisting of pure copper were processed with the condition of femtosecond laser irradiation with the scan rate from 4 mm/s to 20 mm/s and the scan space of 40 µm. The color difference (ΔE) of periodically nano-scaled structure obtained by femtosecond laser irradiation was measured by a multi angle spectrophotometer and quantified by the value of L*a*b* chromaticity diagram. The periodically nano-scaled structures of pure copper showed the roughness (R_a) from 29 nm to 50 nm at the pitch of approximately 280 nm. The brightness was decreased as 15% with an increase of roughness due to a diffused refraction from the surface. The value of L* was ranging from 4 to 81, a* was from 4 to 19 and also b* was from 2 to 24 in the chromaticity diagram of pure copper as detected with tilt angles of 15° to 110°. The calculated ΔE from these results were widely shown from 1.5 to 77, which means that distinctive colors can be realized although the composition of material is not different. It could be expected that the structure color was sufficiently controlled by the periodically nano-scaled structures from femtosecond laser process, and was to be applied at various skin materials.

SS-TuP15 Oxidation of Nb(100) and Kinetics of Surface to Bulk Transport and Extension to Nb_3Sn*, Rachael Farber*, *D.R. Veit, S.J. Sibener,* The University of Chicago

Niobium (Nb) is commonly used in superconducting radio frequency (SRF) accelerator cavities due to its ultra-low surface resistance (R_s) and high cavity quality factor (*Q*) at ~ 2 K. Nb cavities are, however, highly susceptible to localized surface heating, resulting in quenching of the superconducting properties. To minimize quenching, much work has been done to understand factors influencing SRF cavity performance for the clean and oxidized Nb surface. In this work, we have investigated the structural evolution of oxidized Nb(100) under ultra-high vacuum (UHV) conditions to elucidate the structural evolution of the (3×1)-O ladder structure following exposure to O_2. Auger electron spectroscopy (AES) was used to determine oxygen coverage and surface structure was determined using scanning tunneling microscopy (STM). The (3×1)-O Nb(100) surface was exposed to O_2 at 300 K and annealed to various substrate temperatures to facilitate oxygen dissolution. Dissolution kinetics elucidated the surface to bulk oxygen transport mechanism. STM showed the decomposition of the ordered (3×1)-O ladder structure during oxygen dissolution, indicating the importance of oxygen concentration on surface structure. As the fundamental limits of Nb SRF cavities are being realized, it is crucial that alternative SRF materials be studied. Nb_3Sn has been identified as a most promising next generation SRF material with higher *Q* as well as the ability to operate at much higher temperatures, greatly reducing cryogenic infrastructure costs. Ongoing work is focusing on developing preparation methods leading to more homogeneous Nb_3Sn films. *In situ* Sn doping on (3×1)-O Nb(100) combined with surface sensitive techniques such as AES, XPS, and LT-STM will hopefully allow for the diffusion mechanism for Sn on Nb to elucidated, leading to improved procedures for Sn infusion and materials growth.

Tribology Focus Topic
Room Hall B - Session TR-TuP

Tribology Focus Topic Poster Session

TR-TuP1 Measurements of Microscale Friction on Molybdenum Disulfide using an Integrated Quartz Crystal Microbalance and Nanoindentation System*, Brian Borovsky*, *G.R. McAndrews, R.J. Wieser,* St. Olaf College

We report on experiments investigating the microtribological properties of molybdenum disulfide (MoS2) crystals in the high-speed regime. The sliding speeds obtained are over 1 m/s, corresponding to a practical range for mechanical devices. The contacts formed are approximately 1 µm across or smaller. Measurements are performed with a shear-mode quartz crystal microbalance (QCM) integrated into a nanoindentation system. For each test, a thin MoS2 crystal is adhered to the surface of a gold-coated QCM sensor and mechanically exfoliated. The resonant frequency and quality factor of the modified QCM undergo shifts when a spherical sapphire probe is loaded onto the top surface, allowing the detection of lateral contact forces. The shearing amplitude of the QCM is swept over its available range, with the load held fixed, to observe the transition from partial slip to full slip conditions. The contact area is inferred from the lateral stiffness at low amplitudes. We discuss the observed trends in the friction vs. load and area vs. load curves, as well as the degree to which the frictional shear strength depends on mean applied pressure. These results are compared to existing work on MoS2 for contacts ranging from nanometers to millimeters in size, with the aim of contributing to an improved multiscale understanding of tribological phenomena.

TR-TuP2 Sliding Wear Behavior of Tool Steel Functionalized with Organic Monolayers Against Aluminum*, **Stephan Prünte**, D. Music,* RWTH Aachen University, Germany*; V.L. Terziyska, C. Mitterer,* Montanuniversität Leoben, Austria*; J.M. Schneider,* RWTH Aachen University, Germany

Tool steel surfaces were functionalized with methyl-terminated monolayers of phosphonic acids firmly attached by an intermediate metal-oxide adhesion layer. Their sliding behavior against aluminum was investigated with a ball-on-disc tribometer. Our results show a 3-fold reduction of friction and wear for a densely functionalized tool steel with an intermediate Cu–O adhesion layer compared to a non-functionalized sample due to small interactions between Al and the distal methyl moieties of the monolayer. However, functionalized Fe-O adhesion layers on tool steel failed to improve the sliding behavior against Al. This distinct difference may be rationalized by density functional theory calculations. The molecular monolayer attachment to the Cu-O adhesion layer yields 30% higher bond strength compared to one containing Fe-O. Hence it may be speculated that macroscopic sliding wear behavior is determined by the bond strength between the molecular monolayer attachment and the intermediate metal-oxide adhesion layer (on tool steel).

Vacuum Technology Division
Room Hall B - Session VT-TuP

Vacuum Technology Division - Poster Session

VT-TuP1 Characterization and Imaging of Surface Acoustic Waves on GaAs with Raman Spectroscopy*, **Brian Rummel**,* University of New Mexico*; M.D. Henry,* Sandia National Laboratory*; S.M. Han,* University of New Mexico

Surface acoustic wave (SAW) devices are commonly found in sensors and RF filters, and utilizing a facile technique to image the transmitted signal would prove useful in characterizing device operation and optimization. We show how Raman spectroscopy can offer analytical insight into the mechanical strain imposed by SAWs traveling along the surface of various III-V substrates. SAWs are generated using a single port interdigital transducer (IDT) design, modified to produce free surface standing waves. These standing waves provide a means to differentiate between nodes and antinodes of the acoustic wave. The temporal period of the SAWs does not easily allow *in-situ*, real-time measurement of the waves; however, a broadening of the Raman peaks corresponds to an averaging of the peak shifts over the integration time of the spectrometer. An analytical fitting model has been derived to effectively calculate the maximum strain induced by the acoustic waves, thus allowing one to characterize the SAWs. IDTs were deposited onto a GaAs (110) substrate to study the potential of Raman analysis for SAW devices. Wavelengths ranging from 3.2 µm to 10 µm were used to study insertion loss, attenuation, diffraction parameters, and the mechanical coupling coefficient. Future applications of this technique to probe growth defects in ScAlN/Si substrates will also be discussed.

VT-TuP2 Sapphire MEMS based Capacitance Manometer for Vacuum Freeze-Drying Device*, **Masashi Sekine**, M. Soeda, T. Ishihara, M. Nagata,* Azbil Corporation, Japan

New capacitance manometer which has high durability against Clean in Place (CIP) and Sterilization in Place (SIP) cleaning processes for vacuum-freeze drying equipment have been developed.

Vacuum-freeze drying equipment used for manufacturing of medicines or fine chemicals, CIP and SIP processes must be executed to ensure the sterilization of inside of the equipment according to International Organization for Standardization (ISO). The first CIP process, equipment inside is cleaned by water splay at room temperature and then cleaning is followed by SIP process with water vapor of 200-300kPa. To ensure whole cleaning, devices attached to equipment cannot be removed from the equipment. Also protecting valves for devices are not allowed because that inside of devices must be cleaned and stabilized. Therefore devices for these application should have durability of these water spray or vapor environments. Generally pressure range of a manometer for vacuum-freeze drying process is 100Pa absolute and it is heated up to 125 degree C for sterilization.

Authors have developed entirely sapphire-based capacitive pressure sensor chips utilizing MEMS (Micro Electro Mechanical Systems) processes, which are operated at up to 200 degree C with from 0-13 to 0-133k Pa pressure range mainly for semiconductor manufacturing. Cross sectional view of sensor package is shown in Fig.1. Cross sectional view of sensor chip is shown in Fig.2. Deformation of sapphire diaphragm due to pressure change is measured as capacitance change between sensor diaphragm and base-plate.

In the process of adopting this manometer into vacuum-freeze drying process, zero point shifts were found after CIP and SIP processes. Detailed investigation revealed the mechanism of these zero shifts as follows.

Once CIP and SIP processes are conducted, sensing diaphragm is contacting onto base-plate due to over pressure load, such as atmospheric pressure or 200-300kPa. Then diaphragm is mechanically deformed due to temperature change caused by cleaning water or devolatilized vapor. Then diaphragm slides on base-plate to cause friction. Since sapphire is highly electrically insulating material, this friction results in charg ing up on contacted surface s of diaphragm and base - plate (Fig.3).

To solve this problem, we have developed a new electrode configuration which discharges static electricity. Also, improved diaphragm and sensor package structure to suppress thermal deformation have been designed (Fig.4). In actual CIP and SIP processes with this improved sensor structure, the zero point shifts were reduced to under 0.1% Full Scale, which is sufficient for this application (Fig.5).

VT-TuP3 Development of Vacuum Equipment Trainer (VET) Systems for Off-site Students*, **Delmer Smith**, N. Louwagie,* Normandale Community College

While the shape of the Internet of Things (IoT) is still evolving for manufacturers and consumers, its arrival is not in doubt. In addition to a strategic research and development plan, businesses must have a workforce with the knowledge and skills to respond to new directions. Normandale Community College in Bloomington, Minnesota, offers a 12-credit Vacuum Technology Certificate that can be completed in a year. The Vacuum and Thin Film Technology program (Part of the Engineering Technology Department) has provided local education in vacuum science for over 20 years at Normandale Community College. Utilizing technology and curriculum developed with the support of the National Science Foundation division of Advanced Technological Education (DUE 1400408 and Due 1700624), the college now has the capability to reach students at multiple locations throughout the United States. Courses are delivered locally or via a telepresence interface to students throughout the United States. Students receive hands-on practice with Vacuum Equipment Trainer (VET) systems. The VET systems are modular. As students progress through courses, capability is added to increase system functionality. Normandale Community College currently has eight copies of the VET systems. This means that students, both onsite and offsite, can complete a Vacuum Technology Certificate in a year. The first remote student certificates were awarded in the spring of 2018. This paper describes the VET system functionality and how it is used to support the technical content students learn in class.

VT-TuP4 Vacuum System of the SuperKEKB Main Ring in the Phase - 2 Commissioning*, **Yusuke Suetsugu**, K. Shibata, T. Ishibashi, M. Shirai, S. Terui, K. Kanazawa, H. Hisamatsu,* KEK, Japan

The SuperKEKB is an electron-positron collider with asymmetric energies in KEK aiming a high luminosity of 8×10^{35} cm^{-2} s^{-1}. The main ring (MR) consists of two rings, that is, a positron ring with an energy of 4 GeV (Low Energy Ring, LER) and an electron ring with 7 GeV (High Energy Ring, HER). Both rings have the same circumference of 3016 m. In the Phase-1 commissioning from February to June 2016, the vacuum system of the MR worked well as a whole at stored beam currents of approximately 1 A. However, several problems were found, and various countermeasures were taken against these during a long shutdown period before starting the Phase-2 commissioning. For example, permanent magnets were placed around the beam pipes to suppress the electron cloud effect (ECE) in the LER. Other than these works, new beam pipes and components were installed in the main ring, such as six beam collimators required for reducing the background noise of the particle detector. The Phase-2 commissioning of the MR started in March and will be continued until July 2018. By the end of April, the total beam dose (integrated beam currents) are approximately 52 Ah and 57 Ah, and the maximum beam currents are 0.32 A and 0.26 A for the LER and HER, respectively. The pressures recovered soon after starting the commissioning to the level at the final stage of Phase-1 commissioning, and further decreased steadily. The pressure rise normalized by a unit beam current are approximately 1×10^{-6} Pa A^{-1} and 2×10^{-7} Pa A^{-1} for the LER and HER, respectively. The beam lifetime of the HER is approximately 500 min. at 0.22 A, and is almost determined by vacuum pressure. On the other hand, that of the LER, approximately 90 min. at 0.3 A, seems to be mainly limited by the Touschek effect rather than the vacuum pressure. The results of various countermeasures taken in the shutdown period and the effect of permanent magnets or solenoids against the ECE will be investigated soon. The performances of the new vacuum components will be also checked at higher beam currents. Reported here will be the status and the major results of the vacuum system of the MR during the Phase-2 commissioning, and problems for the next Phase-3 commissioning.

VT-TuP5 Smart Diagnostics for Dry Vacuum Pumps Running in Semiconductor Processes*, **Wan-Sup Cheung**, J. Lim,* KRISS, Republic of Korea*; N.K. LEE, J.B. LEE, T.J. Park, T.H. Kim,* SK Hynix, Republic of Korea

This paper addresses logical and smart ways of diagnosing the operation conditions of dry vacuum pumps in the semiconductor processes of the SK Hynix company. In the last four years, SK Hynix has been attempting to complete the ‘production data logging’ systems, including even the collection of the state variables of dry vacuum pumps running in the semiconductor processes. Recent attempts have been added to exploit the logged state variables to diagnose individual dry vacuum pumps operating in the highly tough and risky production processes since their failures always accompany much time and cost. Adaptive parametric modelling (APM) approaches developed by the KRISS research team were considered to analyze the trend and statistical properties of the logged state variables of vacuum pumps. APM approaches are illustrated to provide merits of dramatic (more than 100 times) data reduction for the construction of ‘normal operation condition (NOC)’ reference batches from the beginning part of the logged state variables. The singular value decomposition (SVD) is exploited to decompose the selected NOC reference batch matrix into the sore and projection matrices, which are shown to enable the evaluation of two diagnostic indicators for each vacuum pump, the Hotelling’s T-squared (T2) value and the sum of squared residuals (Q). Both scalar values T2 and Q are demonstrated to play critical roles in diagnosing the current operation conditions of individual vacuum pumps, more specifically the similarity and difference of the current process state in reference to the NOC reference batches. In this work, several attempts have been carried out to improve the reliability and robustness of the diagnosis of vacuum pumps. The use of vibration measurements was the first selected candidate. Field tests are now in progress. It is expected that field test results are to be illustrated in the presentation of this paper.

VT-TuP6 Commissioning of Vacuum System for Positron Damping Ring for SuperKEKB*, **Kyo Shibata**, Y. Suetsugu, T. Ishibashi, M. Shirai, S. Terui, K. Kanazawa, H. Hisamatsu,* KEK, Japan

The SuperKEKB, which is an upgrade of the KEKB B-factory, is a high-luminosity electron-positron collider. To satisfy the requirements of high beam quality for positron injection into the SuperKEKB, a new damping ring (DR) with a circumference of 135.5 m was constructed in an upgraded injector system. The positron beam extracted from the injector linac with an energy of 1.1 GeV is stored in the DR for more than 40 ms, where the beam emittance is damped. Subsequently, the low-emittance beam is extracted and sent back to the linac to be accelerated to 4 GeV and injected into the SuperKEKB. The maximum stored beam current is 70.8 mA.

The vacuum system of the DR is divided into five sections. Main sections are two arc sections with a length of ~110 m in total. Since there is synchrotron radiation irradiation in the arc sections (critical energy: 0.8-0.9 keV), the average pressure over the entire ring during the beam operation is determined mainly by the pressure of the arc sections. The material of the beam pipes is aluminum alloy. The required beam lifetime determined by the residual gas scattering is longer than 1000 sec and it is expected that the average pressure should be lower than $1\text{x}10^{-5}$ Pa. Non-evaporable getter (NEG) pumps are mainly used with auxiliary ion pumps.

The construction of the DR was completed by the end of January 2017. It took more than two weeks from the start of the evacuation process from atmospheric pressure to the end of the activation of NEG pumps because of the small conductance of the beam pipes. The commissioning of the DR commenced in February 2017. When the beam was accumulated for the first time, the pressure exceeded $1\text{x}10^{-5}$ Pa with a beam current of ~1.5 mA. However, the pressure decreased quickly below $1\text{x}10^{-5}$ Pa. Subsequently, the pressure decreased gradually while the beam current was increased. The maximum stored current reached 11 mA on February 23. The residual gas composition of the pressure with the stored beam was typical of that expected for a vacuum system pumped by NEG pumps. Vacuum scrubbing has progressed smoothly thus far, and a beam lifetime of longer than 1000 sec was obtained with a stored beam current of 8 mA, when the beam dose was 0.7 Ah. The pressure distribution in the beam pipes was calculated using the Molflow+, and it is estimated that the photon stimulated desorption rate for CO at that time was reduced to ~$1\text{x}10^{-4}$ molec./photon.

After beam tuning of the DR, the beam injection into the SuperKEKB commenced on March 27. No problems have been identified for the vacuum system to date.

VT-TuP7 Development of a Measurement System for Pressures in Vacuum Regions using an Optical Method*, **Yoshinori Takei**, K. Arai, H. Yoshida, Y. Bitou, S. Telada, T. Kobata,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

Future primary standards of pressure based on optical measurement are being developed in national metrology institutes (NMIs) [1]. Pressure is proportional to refractive index according to both the equation of state of gas and the Lorentz-Lorenz equation. Refractive index can be measured using an optical method based on frequency measurement. Therefore, pressure measurements with a small uncertainty and a wide-range can be achieved. The purpose of this study is developing a pressure measurement system using an optical method for pressure range from 1 Pa to 100 kPa.

A Fabry-Perot interferometer was used for measuring the refractive index of the fulfilled gas in a chamber. The chamber, whose volume was around 7.6 L, was evacuated by a turbo molecular pump and a diaphragm pump. The background pressure and the pressure increase rate after closing the valve were respectively 1×10-3 Pa and 2×10-8 Pa/s, which cause one of uncertainty factors in a low pressure measurement. Pure nitrogen gas was used to fulfill the chamber. The pressure in the chamber was stabilized using a pressure balance from 10 kPa to 100 kPa or by simple accumulating from 1 Pa to 10 kPa. A commercially available external-cavity laser diode (ECLD) was used as frequency-tunable laser light source in order to measure wide-range frequency. The laser frequency was locked to a resonant line of an optical resonator installed in the chamber using the Pound-Drever-Hall (PDH) method. The locked frequency was measured by a beat signal comparing with the reference laser. Aluminum was used as the chamber material to reduce the temperature distribution around the optical resonator. Temperatures of the chamber were measured using several calibrated platinum resistance thermometers and several thermistors. The developed system measured fluctuations in the atmospheric pressure. The evaluated linearity and its uncertainty between refractive index of nitrogen and pressure from 1 Pa to 100 kPa gas are presented.

[1] Jay H. Hendricks et al., ⅩⅩⅠIMEKO,1574-1577, (2015).

VT-TuP8 Study on a Performance of a Sniffer Leak Detector based on EN 14624*, **Kenta Arai**, H. Yoshida,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

Recent years, a portable type sniffer leak detector plays an important role for searching leaks of refrigerant gases from air-coordinators to prevent the global warming. In general, a standard leak, from which a small continuous gas (order of sub-g/year to ten-g/year) flows out, is used to check the performance of the leak detector for a reliable leak test. For the purpose, there are two methods to check the detector. One is that a probe of the detector is moved in front of the standard leak (method A) and the other is that the probe and an exhaust of the standard leak are closed and almost touched (method B). For method A, several standards have been published, i.e., SAE J1627:2011 and its related standards, EN 14624:2012[1], and ANSI/ASHARHE 173-2013. In those standards, the prove velocity and the distance between the probe and the exhaust of the standard leak are given and for EN 14624, 20 mm/s and 3 mm, respectively. For method B, it is explained in a manual of several leak detectors. In this study, we have measured the response of the leak detector against the standard leak by those two methods and compared their results.

A sniffer leak detector in which a pump equipped is tested. For method A, the detector was set on an electric actuator and its probe was set to face an exhaust of a standard leak. The moving velocity of the electric actuator was changed from 5 mm/s to 40 mm/s and the distance between the probe and the standard leak changed from 1 mm to 20 mm. For method B, the velocity was set at 0 mm/s and the distance at 0 mm, respectively. Prior to the tests, the leak rate of the standard leak was calibrated to be 5 g/year by a pressure rise method [2].

Both at the beginning and at the end of the experiments, the response of the leak detector was obtained by method B. Between them, the response of the leak detector was obtained by method A. The detector output obtained by method B between two measurements was stabilized within 10 %. For method A, the detector output was decreased with an increase of both the probe velocity and the distance from the probe to the standard leak. Above both the probe velocity of 20 mm/s and the distance of 10 mm, the detector output was disappeared. The detector output obtained by method B was about 5 times as high as that obtained by method A with the velocity of 20 mm/s and the distance of 3 mm given in EN 14624. Thus, for the properly use of the sniffer leak detector, it is important to clear the conditions for its performance check.

[1] EN 14624:2012 Performance of portable leak detectors and of room monitors for halogenated refrigerants.

[2] Kenta ARAI *et al*., Metrologia **51** (2014) 522.

VT-TuP9 Elimination of Electron-Beam-Induced Carbonaceous Contamination in SEMs and the new RGM 10100 NIST Contamination Testing Artifact, ***Andras Vladar,*** *K. Purushotham,* National Institute of Standards and Technology (NIST)

Electron and ion beam-induced contamination could be a severe problem of scanning electron microscopes. The carbonaceous material deposited in a dynamic process of adsorption and desorption at the irradiated area can easily disturb imaging and lead to erroneous measurement results. The sources of contamination are usually both the SEM and the sample. Cleaning of the SEM can be carried out with a low-energy (oxygen) plasma cleaning process using commercial devices [1], but without a for-sure-clean sample, it is not possible to determine whether potentially time-consuming cleaning of the SEM is indeed necessary. The RGM 10100 sample with its associated cleaning and evaluation procedures, combined with appropriate cleaning processes offer an effective solution for this problem.

Figure 1 in the supplement shows three levels of SEM cleanliness. The energetic primary electrons can “purge” the center of the sample from carbonaceous contaminant molecules. The center brightening is due to slight oxidation caused by electron irradiation at 40 times the typical dose. With a clean RGM 10100 in a SEM there is no perceivable carbonaceous contamination even after many hours of continuous electron bombardment.

RGM 10100 can be cleaned with acidic piranha solution and can stay clean for months in a semiconductor grade plastic container. The necessary SEM cleaning time, depending on the cleanliness of the SEM, varies from 10 minutes to a couple of days. It is common that the contamination “comes back” after some time. As the SEM gradually becomes free of the source molecules of contamination, the time between needed cleanings could increase to months. RGM 10100 is available from the NIST Office of Reference Materials.

[1] http://evactron.com [http://evactron.com/], http://ibssgroup.com [http://ibssgroup.com/], http://www.piescientific.com [http://www.piescientific.com/]

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VT-TuP11 Extreme 2 Million Liter/sec Hydrogen Pump Speed Measurements of C-2W Divertors, ***Ernesto Barraza-Valdez,*** *A. Van Drie,* TAE Technologies

TAE Technologies (TAE) has completed building and commissioning its latest machine, C-2W. C-2W has four 15m3 divertors which require the capability to pump out H2 neutral particles at a rate of 2,000 m3 /s and D2 neutral particles at 1,500 m3 /s. To achieve this, TAE has developed LN2 cooled titanium getter cryobox pumps each with a pump speed of approximately 110 m3 /s and 85 m3 /s for hydrogen and deuterium respectively. These cryoboxes are arrayed in the divertors to achieve the high pump speeds required to keep the plasma conditions optimal during C-2W operations. Experimental pump speed and density measurements using fast ion gauges and residual gas analysis of C2W’s four divertors will be presented.

VT-TuP12 KICT Dirty Thermal Vacuum Chamber: design, fabrication, and performance test, *T. Chung,* Korea Institute of Civil Engineering and Building Technology, Republic of Korea*;* ***Jong Yeon Lim,*** Korea Research Institute of Standards and Science, Republic of Korea*; Y. Yoo, hss. Shin,* Korea Institute of Civil Engineering and Building Technology, Republic of Korea

KICT is designing and building a large thermal vacuum chamber with a simulant regolith test bed inside, named Dirty Thermal Vacuum Chamber (DTVC), capable of performing characteristics evaluation of extraterrestrial exploration drill tools, rovers, and 3D printing tools , as well as investigating the physics and effects of thermal radiation. The DTVC system consists of a D-shape main chamber, ϕ 4 m x 4 m, and a preliminary chamber of ϕ4 m x 2 m enabling of preparing and conditioning samples. The extension of the simulant bed to 6 m in length is also possible with opening the gate valve between two chambers for a rover maneuvering test through both chambers.

To successfully establish the DTVC system, a vacuous, cryogenic, and anhydrous (no water) soil environment, simulation of the lunar and Mars surfaces was first proposed with physics requirements of -190 ^{o}C ~ 150 ^{o}C in the pressure range of 10^{-4} mbar ~ 10^{-5} mbar. In order to realize the desired pressure of 5 x 10^{-8} mbar without any components inside, the baseline exhaust system has been equipped with two 2,000 L/s TMPs and two 28,000 L/s cryopumps as well as one 3,000 m^3/h roots pump for roughing and two 300 m^3/h dry pumps for backing. The s amples then can be exposed to thermal radiation on the simulant regolith with UHV background vacuum quality.

Since about 25 tons of simulant regolith are necessary for the bed, the regolith outgassing rate of <5 x 10^{-8} mbar.L/(s.g) is to be strictly regulated to satisfy the physics requirement. For this purpose a smaller scale chamber, called Pilot DTVC, was simultaneously built to realize the outgassing rate of the regolith. An amount of 125 kg of KLS-1, simulant regolith developed by KICT, was pumped down to about 0.1 mbar to remove water content down to <1 x 10^{-4} mbar.L/(s.g). Previous TDS study of the KLS-1 regolith shows the most content of the regolith ingredient adsorbed is water, and the H_2O dose was about 1.2 x 10^{5} mbar.hours during nine month exposure to 50 % RH ambient environment at 300 K average.

This presentation will focus on the brief introduction of the vacuum architecture, and design implementations of the DTVC and Pilot DTVD system for both qualitative and quantitative analyses to satisfy all the strict vacuum requirements.

2D Materials Focus Topic
Room 201B - Session 2D+AM+EM+NS-WeM
Dopants, Defects, and Interfaces in 2D Materials

Moderator: Eric Pop, Stanford University

8:00am **2D+AM+EM+NS-WeM1 Carbon Doping of 2D Transition Metal Dichalcogenides by Plasma Enhanced CVD***, **Yanfu Lu**, F. Zhang, S. Sinnott, M. Terrones,* The Pennsylvania State University

Doping of 2D transition metal dichalcogenides has been discovered to be an effective way to tune the electronic structure and modify the lattice structure at the surface. The n-type and p-type doping of monolayer MoS_2/WS_2 heterostructures may enable the fabrication of field-effect transistors of ultra-low thickness. Plasma enhanced chemical vapor deposition provides a stable and controllable approach for introducing carbon dopants to monolayer WS_2. Photoluminescence measurement indicates that the band gap of C-doped WS_2 decreases by 0.17 eV. Corresponding first principles calculations provide the correlation between the position and chemical saturation of the carbon dopants and the electronic structure of the system. To verify covalently bonded dopants, we use Raman spectroscopy, X-ray photoelectron spectroscopy, and scanning transmission electron microscopy to examine the pristine sample and carbon-doped samples. Subsequent I-V characteristics measurements prove p-type doping and the energy band diagram. Finally, the mechanism associated with and, more importantly, the structure-property relationship of chalcogen doping are analyzed. The resulting new insights of transition metal dichalcogenide-based heterostructures and alloys are discussed.

8:20am **2D+AM+EM+NS-WeM2 Methoxy Formation Induced Defects on MoS_2****, **Duy Le**,* University of Central Florida*; P. Evans,* University of Nebraska - Lincoln*; Z. Hooshmand,* University of Central Florida*; T.B. Rawal,* Oak Ridge National Laboratory*; L. Bartels,* University of California, Riverside*; P.A. Dowben,* University of Nebraska-Lincoln*; T.S. Rahman,* University of Central Florida

Defects are known to play an important role in determining the chemical properties of otherwise inert MoS_2 basal plane. Here we report our joint experimental and theoretical study of the adsorption and reaction of methanol on the MoS_2 basal plane to determine the factors that control system reactivity. We find that exposure of the MoS_2 basal plane to methanol leads to the formation of adsorbed methoxy and coincides with sulfur vacancy generation and that the methoxy moieties bind to molybdenum, not sulfur, while some adsorbed methanol is readily desorbed near or slightly above room temperature. Our calculations also suggest that the dissociation of methanol via O–H bond scission occurs at the defect site (sulfur vacancy), followed subsequently by formation of a weakly bound H_2S species that promptly desorbs from the surface with creation of a new sulfur vacancy, in great agreement with photoluminescence and scanning tunneling microscopy data that show clear evidence of the sulfur vacancy creation on the MoS_2 surface, after exposure to methanol [1].

[1] P. Evans et al, J. Phys. Chem. C (2018). DOI: 10.1021/acs.jpcc.8b02053

* Work supported in part by DOE grant DE-FG02-07ER15842

8:40am **2D+AM+EM+NS-WeM3 Defect Engineering of 2D Materials for Advanced Electronic Devices***, **Gwan-Hyoung Lee**,* Yonsei University, Republic of Korea **INVITED**

Two-dimensional (2D) materials have brought a great deal of excitement to nanoscience community with their attractive and unique properties. Such excellent characteristics have triggered highly active researches on 2D material-based electronic devices. New physics observed only in 2D semiconductors allow for development of new-concept devices. Assembly of 2D blocks for van der Waals heterostructures also provide a big playground for engineers and physicists to investigate unprecedented properties of 2D materials and fabricate multi-functional electronic devices. However, atomically thin 2D materials, such as graphene and transition metal dichalcogenides (TMDs), have only two surfaces at top and bottom without a bulk so that they are very sensitive to environment. In other words, properties of 2D materials can be altered easily by surface modification. In this talk, I will show novel approach to fabricate high performance 2D electronic devices by utilizing various surface treatments, such as fluorination and hydrogenation of graphene and layer-by-layer oxidation of MoS_2. When different types of defects, such as *sp*^{3} bonds and vacancies, are induced on the surface of graphene, the electrical properties of graphene can be tuned. With mild plasma treatment, MoS_2 can be oxidized layer-by-layer and monolayer MoS_2 can be fabricated from the multilayer MoS_2. These surface treatment techniques can be used for fabrication of high performance graphene devices and MoS_2 optoelectronic devices. Defect engineering of 2D materials holds a great promise in engineering the 2D materials and fabricating advanced electronic devices of 2D materials.

9:20am **2D+AM+EM+NS-WeM5 Modeling Defects and Electron-electron Interactions in Low-dimensional Materials***, **Daniel Gunlycke**, C.E. Ekuma,* U.S. Naval Research Laboratory

While each nanoscale structure in a low-dimensional material can exhibit a variety of properties, the odds are that it will be (1) sensitive to defects and (2) strongly influenced by electron-electron interactions. The ratio of defect sites to pristine sites naturally increases, as structures become smaller. Electron localization can furthermore dramatically magnify the role of defects. In low-dimensional materials, dielectric screening is generally less effective, reducing the tendency for electronic interactions to become uniform across the sites in the materials. Despite the importance of both defects and electron-electron interactions, the properties of low-dimensional materials are often investigated in the absence of one or the other. This not only creates uncertainty over the predictions but could entirely miss certain physical phenomena, including insulator-to-metal transitions. In this presentation, we will discuss a general first-principles-based approach to explore realistic low-dimensional structures that explicitly accounts for both defects and electron-electron interactions [1]. It is based around a generalized Anderson Hamiltonian and applies density functional theory, as well as dynamical mean-field theory. We will also present electronic and optical properties of two-dimensional materials obtained using our method and discuss the potential for using defect engineering for improved solar cell performance.

[1] C. E. Ekuma, V. Dobrosavljevic, and D. Gunlycke, *Physical Review Letters* **118**, 106404 (2017)

This work was supported by the Office of Naval Research, directly and through the U.S. Naval Research Laboratory.

9:40am **2D+AM+EM+NS-WeM6 Post-Synthesis Modifications of Two-Dimensional $MoSe_2$ or $MoTe_2$ by Incorporation of Excess Metal Atoms into the Crystal Structure***, **Paula Mariel Coelho**,* University of South Florida*; H. Komsa,* Aalto University, Finland*; H. Coy Diaz, Y. Ma,* University of South Florida*; A.V. Krasheninnikov,* Institute of Ion Beam Physics and Materials Research, Germany*; M. Batzill,* University of South Florida

Modifications of $MoSe_2$ and $MoTe_2$ with metallic mirror twin grain boundaries (MTB) in films grown by molecular beam epitaxy have been previously reported [1,2]. The goal of the study presented here has been to understand the formation-mechanism of MTB networks and apply this gained knowledge for controlled modifications of these 2D materials. In a combined scanning tunneling microscopy and density functional theory approach we demonstrate that excess Mo can easily diffuse into the pristine $MoSe_2$ or $MoTe_2$ (but not into MoS_2) layer and cause crystal modifications into Mo-rich twin grain boundaries. Vapor deposited Mo atoms are first incorporated by diffusing into interstitial (or split-interstitial) sites. Then, further Mo-atoms incorporate into the crystal structure to form triangular, Mo-rich grain boundary loops. Only after a critical density of MTBs is reached, Mo is no-longer absorbed by the 2D-crystal sheet and Mo-clusters start to form at the surface. The energetics and barriers for Mo-incorporation is calculated by DFT and shows that the formation of twin grain boundaries in the presence of excess Mo is favorable for $MoTe_2$ and $MoSe_2$, but not for MoS_2 - in agreement with the experiment. The achievable dense networks of MTBs constitute a new Mo-rich metallic phase that may be used for controlled electric contacts or creation of active sites in electro-catalysis [4] and thus adding new functionalities into transition metal dichalcogenide-based materials and devices. Moreover, DFT simulations suggest that this mechanism for incorporation of transition metals is not limited to Mo. This enables modification of the materials properties by heteroatom dopants and initial experimental work demonstrates the incorporation of both Ti and V. V-interstitials in $MoTe_2$ are predicted to have a magnetic moment and magnetic hysteresis curves indicate the induction of ferromagnetism in $MoTe_2$ by doping the material with less than 1% of V interstitials.

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[3] Ma Y. et al. (2017) Angle resolved photoemission spectroscopy reveals spin charge separation in metallic MoSe2 grain boundary. Nat. Commun. 8, 14231.

[4] Tomasz Kosmala et al. (2018) Metallic Twin Boundaries Boost the Hydrogen Evolution Reaction on the Basal Plane of Molybdenum Selenotellurides. *Adv. Energy Mater.* 2018, 1800031.

11:00am **2D+AM+EM+NS-WeM10 Dry Cleaning and Doping of MX₂ for Contact Engineering***, **Daniil Marinov**,* IMEC, Belgium*; J. Ludwig,* IMEC & KU Leuven, Belgium*; D. Chiappe,* IMEC, Belgium*; E. Voronina, T. Rakhimova,* Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University*; J.-F. de Marneffe, I. Asselberghs,* IMEC, Belgium*; S. De Gendt,* IMEC, KU Leuven, Belgium

Two-dimensional transition metal dichalcogenides (e.g. MoS_2, WS_2) are promising materials for a number of electronic and optoelectronic applications. Wafer-scale integration of these materials into sophisticated devices requires atomic-scale control of the processing steps such as deposition, etch, clean and doping. Reduction of the contact resistance is a major roadblock towards demonstration of high-performance devices. Significant Schottky barrier at the metal-MX_2 interface as well as surface contamination (e.g. by polymer residues) are the main factors contributing to the high contact resistance in fabricated MX_2 devices. In this study, a fully dry cleaning and doping technique is developed with a particular focus on contact engineering.

We demonstrate that a remote H_2 plasma is efficient for removal of organic residues from MX_2 surfaces. However, sulfur can be also stripped from the topmost layer by reactive H atoms. The main challenge is thus to precisely control the sulfur loss while maintaining the cleaning efficiency. At high substrate temperature, a 200 nm PMMA layer can be fully removed selectively to a single layer of WS_2 without damaging the 2D material (as confirmed by photoluminescence measurements). At low substrate temperatures significant S-vacancy formation was observed. Surface temperature is therefore the key parameter for controlling the reactivity of H atoms on WS_2.

Controllable formation of sulfur vacancies opens routes for substitutional doping. After H_2 plasma strip, WS_2 and MoS_2 samples were exposed to a flow of molecular gases (Cl_2, CO, OCS) without igniting the plasma. It is shown that Cl_2 and OCS can react with H_2 plasma treated MX_2 forming stable surface groups. Ex-situ conductive AFM measurements confirm that molecular doping prevents the loss of conductivity (that is observed after H_2 plasma alone). Moreover, OCS and Cl_2 exposure enhances electrical current injection in the material through grain boundaries and edges. The latter effect is beneficial for contact resistance reduction on MX_2.

To gain a deeper insight in the observed surface phenomena, DFT simulation of the interaction of atomic (H, Cl, F) and molecular (OCS, Cl_2) species with MX_2 surface was performed. S-vacancy creation by atomic hydrogen via formation of gas phase H_2S was observed in simulations, in qualitative agreement with the experiments. Moreover, dissociative adsorption of Cl_2 and OCS in S-vacancy sites is predicted by the DFT model.

Dr D. Marinov has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 752164.

11:20am **2D+AM+EM+NS-WeM11 Deep Learning for Atomically-Resolved Scanning Transmission Electron Microscopy Experiments on 2D Materials***, **Maxim Ziatdinov**, S.V. Kalinin,* Oak Ridge National Laboratory

Understanding fundamental atomic-scale mechanisms behind solid state reactions and phase transformations is critical for optimizing functional properties of technologically relevant materials. Recent advances in scanning transmission electron microscopy (STEM) have allowed to visualize dynamic processes in solid state systems, induced by thermal or chemical stimuli or electron beam, on the level of individual atoms and single atomic defects. However, while there have been multiple STEM studies on materials structure evolution, the materials-specific knowledge on the kinetics and thermodynamics of these processes and atomic potentials is almost non-existent, which is mainly due to the inherent limitations of the current (semi-)manual image analysis techniques. Here we demonstrate an approach based on deep convolutional neural networks for automated analysis of dynamic STEM data from 2-dimensional materials, such as monolayer WS_2, under e-beam irradiation. Our approach allows to create a library of atomic defects, explore subtle atomic distortions around the defects of interest and map chemical transformation pathways on the atomic level. We specifically show how the developed framework can be used for extracting diffusion parameters of sulfur vacancies in WS_2 and for studying transformation pathways for Mo-S complexes, including detailed transition probabilities.

11:40am **2D+AM+EM+NS-WeM12 Magnetic Doping in 2D MBE-grown-MoSe₂/graphene Heterostructures Studied by Photoelectron Spectroscopy and Band Structure Imaging***, **Maxime Gay**, O.J. Renault,* CEA-LETI, France*; MT. Dau, C. Vergnaud, M. Jamet,* CEA-INAC-SPINTEC, France

2D TMDCs present a unique combination of electronic and mechanical properties such as a direct bandgap, strong spin-orbit coupling and K-valley inequivalence, with an atomic-scale thickness [1]. Introducing magnetic phases into these materials opens exciting perspectives towards spin control in magnetic tunnel junctions. To date, magnetism in 2D systems was mostly studied by theoretical calculations. Within the diluted magnetic semiconductors model, transition metal atoms from the monolayer are substituted by a few Mn, Fe or Co atoms [2-4].

Our study focuses on Mn-doped-$MoSe_2$ monolayers, grown by molecular beam epitaxy on graphene, and characterized by photoemission techniques (XPS, kPEEM) coupled with observations at different scales (DRX, TEM). Before doping, we found that the in-plane lattices of graphene and $MoSe_2$ are aligned with each other and that a bandgap opens in the graphene around the Fermi level [5-6]. After Mn doping, the obtained Mn insertion is measured up to 15% by XPS. The influence of Mn doping on the band structure of $MoSe_2$/graphene heterostructure will be presented and discussed.

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Actinides and Rare Earths Focus Topic
Room 202C - Session AC+MI+SA-WeM

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

Moderators: Melissa Denecke, University of Manchester, UK, James Tobin, UW Oshkosh

8:00am **AC+MI+SA-WeM1 Strong electron-electron Interactions in the Actinides: Using Organometallics to Probe Delocalization Effects***, **Corwin Booth**,* Lawrence Berkeley National Laboratory **INVITED**

Systems exhibiting strong electron-electron interactions remain at the forefront of inquiry into complex properties of condensed matter systems due to their exciting properties (eg. superconductivity) and their resistance to being understood on a fundamental level. A bottleneck toward a better understanding has been the difficulty of the required many-body calculations for extended solids. Alternatively, calculations on small molecules require fewer and better approximations, potentially offering a better description. Although strong electron-electron interactions are well established in extended solids, recent work on lanthanide organometallic coordination compounds has demonstrated the importance of such interactions, fueled by the propensity for certain 4f orbitals to be partially delocalized. Meanwhile, recent work on the actinides challenges the canonical view that the 5f electrons can bond in the light actinides but are essentially localized in the heavier actinides. A major stumbling block for such work is the paucity of known structures for elements beyond Am in the periodic table.

For the discussion presented here, work on Ce and Yb organometallics will provide context in terms of f-occupancy and in bonding characteristics and the effect on magnetism. The role of strongly electron interactions will be described in terms of configuration interaction (CI) and related calculations. Occupancy is measured using Ln L_{III}-edge x-ray absorption near-edge structure (XANES) techniques, and local structure (EXAFS) measurements demonstrate the final effect on the bonding at the metal center. Of particular interest is what happens in formally Ce(IV) systems that exhibit strong interactions.

XANES measurements of actinides are more difficult to interpret and will be discussed. The focus will be, however, on EXAFS measurements across the An series in the presence of strongly oxidizing ligands. Chosen ligands include hydroxypyridonone (HOPO), with less oxidizing ligands, such as diethylenetriaminepentaacetic acid (DTPA) used for comparison. Cations include Th, U, Pu, Am, Cm, Bk, and Cf. Discussions will center on nearest-neighbor bond lengths, using DFT calculations as a guide. The surprising role of covalency in the late actinides will be considered, both in terms of the EXAFS results and in terms of the edge shifts.

This work was supported by the U.S. Department of Energy (DOE), Office of Science (OS), Office of Basic Energy Sciences (OBES), under Contract No. DE-AC02-05CH1123.

8:40am **AC+MI+SA-WeM3 Structure and Magnetism of U-based Thin Films and Heterostructures***, **Evgeniya Tereshina-Chitrova,*** Institute of Physics, Academy of Sciences of the Czech Republic*; L. Havela,* Charles University, Prague, Czech Republic*; T. Gouder, Z. Bao,* Institute for Transuranium Elements, Germany*; M. Dopita,* Charles University, Prague, Czech Republic*; R. Caciuffo,* Institute for Transuranium Elements, Germany **INVITED**

Uranium is the basic component of most nuclear fuels. The production of uranium-based films has advantage over bulk materials studies as it allows performing advanced physics and chemistry experiments on small amounts of radioactive material and on its clean and smooth surfaces. Other interesting field is uranium magnetism. Although uranium itself is non-magnetic, uranium compounds display a rich variety of magnetic phenomena intimately related to the variable character of the 5*f* electron states [1]. Additional degrees of freedom can be used in thin films, in which the reduced dimensionality and structure modifications far exceed the limits imposed by thermodynamics, obeyed in bulk systems. We review the achievements in the field of sputter-deposited films, in which variations of deposition conditions can dramatically suppress crystallinity of the deposited material. The 5f itinerant magnetic systems (as US or UN [2]) react to the low substrate temperatures and high deposition rates by decreasing ordering temperatures and eventually by the loss of U magnetic moments. The strong ferromagnetism of uranium hydride is, on the other hand, almost insensitive, which underlines its local-moment character.

The possibility to combine films of various materials on the nanostructure scale can also give rise to new functionalities. For example, the exchange bias (EB) effect [3], arising as a result of combination of a ferromagnet biased by exchange interaction at the interface to an antiferromagnet, is particularly interesting if uranium magnetics are involved. The new ingredient, strong spin-orbit interaction, can lead to very strong magnetic anisotropy, which represents an essential parameter. We have been systematically studying films of Fe_3O_4 (ferromagnet) grown using different substrates on the top UO_2, playing the role of biasing antiferromagnet [4]. The resulting high bias field (> 0.2 T) and a proximity effect, in which the high Curie temperature of Fe_3O_4 provides the EB functionality even at temperatures exceeding ordering of UO_2, demonstrate the promising aspects of using actinides in this non-traditional way.

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9:20am **AC+MI+SA-WeM5 Field Induced Lifshitz Transitions in URu2Si2***, EJ. Calegari,* Univ Federale Santa Maria, Brazil*; S.G. Magalhaes,* Universidade Federale Rio Grande do Sul, Brazil*; **Peter Riseborough,*** Temple University **INVITED**

We report calculations on an unusual phase of the Under-screened Anderson Lattice (UAL) model, the so called spin-dependent inter-orbital density wave that has been proposed as describing the ``Hidden Order" (HO) phase of URu2Si2.

We determine the effects of an applied magnetic field. Since the order parameter describes an ordering in the x-y plane, the electronic properties of the system are anisotropic below the critical temperature THO. We show that the magnetic susceptibility becomes anisotropic below THO. Furthermore, for fields applied along a spontaneously chosen hard axis, THO decreases towards zero and that the HO transition changes from second order to first order at a large value of the magnetic field. Also, we find that the system undergoes a cascade of field-induced Lifshitz transitions and also show how these properties originate from the dependence of the quasi-particle bands on the orientation of the applied field. The good qualitative agreement with experimental findings provides strong support for the proposed description of the HO phase as a spin-dependent inter-orbital density wave phase.

11:00am **AC+MI+SA-WeM10 New Form of Uranium Hydride - UH_2***, **Ladislav Havela,** M. Paukov, M. Dopita, L. Horak, P. Minarik, M. Divis, I. Turek,* Charles University, Prague, Czech Republic*; D. Legut,* VSB-Technical University of Ostrava, Czech Republic*; T. Gouder, A. Seibert, F. Huber,* European Commission - Joint Research Centre*; E.A. Tereshina-Chitrova,* Institute of Physics, Academy of Sciences of the Czech Republic

Most of *f*-elements form with hydrogen both di- and trihydrides. Actinide and rare-earth dihydrides occur, as a rule, in the CaF_2 structure type. Uranium represents an exception, only UH_3 is present in the binary phase diagram. It exists in two different structure types. The metastable form α-UH_3 forms in the Cr_3Si structure type, which is in fact *bcc* U lattice filled with hydrogen. The stable form β-UH_3 has a larger cubic cell with two different U sites. Both forms are ferromagnets with the total U moment of $\approx 1\ \mu_B$/U and the Curie temperature $T_C \approx 165$ K. We have recently synthesized UH_3 thin films using a reactive sputter deposition. XRD analysis indicated the β-UH_3 structure, modified by a pronounced (00l) texture and compressive residual strains imposed by the deposition dynamics. Magnetization measurements proved $T_C = 165$ K.

The sputter deposition on a cooled substrate ($T = 170$ K) using Si wafer the crystal structure turned different. The deposited material is undoubtedly cubic, of the *fcc* type, and the lattice parameter $a = 5.3598 \pm 0.0014$ Å is very close to that of PuH_2 ($a = 5.359$ Å) and NpH_{2+x} ($a = 5.343$-5.355 Å). Hence we can assume that UH_2 in the fluorite structure has been formed. The key role in stabilization plays likely the effect of substrate (Si has $a = 5.431$ Å) in combination with low temperature deposition. The UH_2 film was subsequently subjected to magnetization measurements, which indicated a ferromagnetic ground state with $T_C \approx 125$ K. This is lower than in the UH_3 phases, although the U-U spacing in UH_2 should be higher, 3.78 Å, than in both UH_3 phases (3.31 and 3.60 Å for β- and α-UH_3, respectively). This fact points to the U-U interaction being more important than the U-U spacing. The ferromagnetic state is also the ground state obtained from ab-initio calculations. Scalar relativistic calculations (LDA) for experimental lattice parameter yield the spin moment $\mu_S = 2.0\ \mu_B$/U. LDA+U (U = 2.25 eV) gives the equilibrium lattice parameter $a = 539.9$ Å, i.e. 0.7% larger than the experimental one, the ferromagnetic ground state with (111) easy-magnetization direction and the magnetic anisotropy energy $E_a = 9$ meV. The total moment 0.45 μ_B/U consists of 2.59 μ_S and -3.04 μ_L.

This work was supported by the Czech Science Foundation under the grant No. 18-02344S. The work at JRC Karlsruhe was supported by the European FP7 TALISMAN project, under contract with the European Commission. Part of the work was supported by the project "Nanomaterials centre for advanced applications", Project No. CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF.

11:20am **AC+MI+SA-WeM11 Tuning of Electronic Properties of U- and RE-Metallic Systems by H Absorption***, **Silvie Maskova,*** Charles University, Prague, Czech Republic*; K. Miliyanchuk,* Ivan Franko National University of Lviv, Lviv, Ukraine*; A. Kolomiets,* Lviv Polytechnic National University, Lviv, Ukraine*; L. Havela,* Charles University, Prague, Czech Republic

The sensitivity of the interactions in the intermetallic systems to modification of the crystal structure makes the experimental techniques involving alteration of the atomic arrangement especially important. Various studies under compression are well-known examples of such methods. From this point of view hydrogenation can be treated as a complementary technique that provides „negative" pressure. Hydrides can be defined as compounds for which the hydrogen absorption leads to the modifications of the crystal structure, such as pure lattice expansion or the formation of a new structure. As a result, the new compounds (hydrides) exhibit qualitatively new physical properties and such modifications provide us with additional information on the peculiarities of interatomic interactions in the initial compounds.

As an example, we will compare the impact of H absorption on U- and RE-compounds using A_2T_2X (A = Rare-Earth (RE) or actinide, T = transition metal, X = *p*-metal) compounds crystallizing in the tetragonal Mo_2FeB_2 structure type (space group *P4/mbm*). U_2T_2X interact with H_2 only at high pressure (≈ 100 bar) reaching 2 H/f.u. The H absorption produces a lattice expansion (lower than 10 %), while the tetragonal structure is preserved.

Higher H concentrations, which can be achieved in some RE_2T_2X compounds (up to 8 H atoms/f.u), lead to amorphization or structure symmetry changes (with volume expansion exceeding 20 %), imposed by a minimum H-H distance requirement.

Magnetic properties of U-compounds strongly depend on the U-U distances. Hydrogen intrusion modifies the lattice by expanding it without changing the crystal-structure type leading to a 5*f* band narrowing. As a consequence, doping of U intermetallics by interstitial hydrogen leads to stronger magnetic properties. On the other hand, the hydrogen absorption has opposite effect on magnetic properties of RE_2T_2X compounds. For RE compounds, hydrogenation affects mainly the inter-site exchange interaction, which is weakened presumably by reducing the concentration of conduction electrons, responsible for the RKKY interaction.

11:40am **AC+MI+SA-WeM12 Magnetic Structures of U_nRhIn_{3n+2} Materials***, **Attila Bartha**, M. Klicpera,* Charles University, Prague, Czech Republic*; P. Cermak,* Forschungszentrum Juelich GmbH, Germany*; B. Ouladdiaf,* Institute Laue-Langevin, France*; J. Custers,* Charles University, Prague, Czech Republic

In the past decade, U-compounds crystallizing in the $HoCoGa_5$-type structure (P4/*mmm*), frequently referred to as 115, have been in the focus of attention in experimental and theoretical research. Vigorous activities have been motivated by the high superconducting transition temperature of T_c = 8.7K in $PuRhGa_5$ [1] and T_c = 18.5K in $PuCoGa_5$ [2]. No further superconductivity has been reported in neither U-115 nor in the closely related U_2TGa_8 compounds (T = transition metal). However, interesting magnetic properties have been observed: neutron scattering experiments revealed that $UNiGa_5$ exhibits the G-type antiferromagnetic (AFM) phase, while $UPdGa_5$ and $UPtGa_5$ exhibit the A-type AFM state. Note that G-type indicates a 3D Néel state, while A-type refers to a layered AF structure where spins align FM in the *ab* plane and AFM along the c axis [3]. The difference in the two magnetic structures is significant since it implies a sign change of the nearest-neighbor (NN) interaction.

Here we report on the magnetic structures of $URhIn_5$ and U_2RhIn_8, two new members of the $U_nT_mX_{3n+2m}$ (X=In,Ga) family of compounds [4]. $URhIn_5$ displays AFM order below T_N = 98K. The observed increase of the resistivity for current parallel [100], [110] and [001] are reminiscent to a spin-density wave (SDW) type of transition with the gap opening first along the [001] direction [5]. U_2RhIn_8 enters the AFM state at T_N = 117K. No increase in resistivity in the vicinity of T_N is found which would hint to a SDW gap opening. Neutron diffraction experiments on $URhIn_5$ were performed at the Heinz Maier-Leibnitz Zentrum (MLZ) in Garching using the triple axis spectrometer PANDA. Single crystals with accumulated mass of 10mg where glued on an Al-plate. Our results confirmed the magnetic propagation vector ***k***=(1/2,1/2,1/2) predicted by NMR experiments [6] and a magnetic moment of 1.65 μ_B/U^{3+}. The neutron study on U_2RhIn_8 has been conducted at ILL, Grenoble using D10 on only one single crystal with $m \approx$ 1mg. Analysis revealed a propagation vector ***k***=(1/2,1/2,0) and an ordered moment of 1.7 μ_B/U^{3+}. UIn_3, $URhIn_5$ and U_2RhIn_8 all show G-type AFM phase. While the *c*-axis parameter differs significantly the *a* lattice parameter equals 4.601Å, 4.621Å and 4.6056Å respectively, being a change of less than 1% pointing to the fact that the NN coupling is important for the type of magnetic structure.

[1] F. Wastin *et al.*, J.Phys.Condens.Matter **15,** S2279 (2003)

[2] J.L. Sarrao *et al.,* Nature (London) **420,** 297 (2002)

[3] T. Hotta, Phys.Rev. B **70,** 054405 (2004)

[4] A. Bartha *et al.*, J.Magn.Magn.Mater. **381,** 310 (2015)

[5] A. Bartha *et al.*, Acta Phys.Pol. A **127,** 339 (2015)

[6] H. Sakai *et al.* Phys.Rev. B **88,** 045123 (2013)

12:00pm **AC+MI+SA-WeM13 Insights into the Magnetic Dead Layer in $La_{0.7}Sr_{0.3}MnO_3$ Thin Films from Temperature, Magnetic Field and Thickness Dependence of their Magnetization***, **Navid Mottaghi**, S. Seehra, R. Trappen, S. Kumari, C.-Y. Huang, S.F. Yousefi, G.B. Cabrera, A. Romero, M.B. Holcomb,* West Virginia University

Detailed dc magnetization (M) measurements of a 7.6 nm $La_{0.7}Sr_{0.3}MnO_3$ thin film samples is investigated. The sample was fabricated by pulsed laser deposition. Zero-field-cooled (ZFC) M vs. applied field (H) cooled down to T = 5 K reveal the presence of negative remanent magnetization (NRM) as well as in ZFC M vs. temperature (T) measurements in H = 50 Oe and 100 Oe. ZFC and FC (field-cooled) protocols are used to determine the blocking temperature T_B in different H. Isothermal hysteresis loops at different T are used to determine the temperature dependence of saturation magnetization (M_S), remanence (M_R) and coercivity H_C. The M_S vs. T data are fit to the Bloch law, $M_S(T) = M_0(1 - BT^{3/2})$, showing a good fit for $T <$ 100 K and yielding the nearest-neighbor exchange constant $J/k_B \cong 18$ K. The variations of T_B vs. H and H_C vs. T are well described by the model often used for randomly oriented magnetic nanoparticles with magnetic domain diameter ≈ 9 nm present in the dead-layer of thickness d =1.4 nm. Finally, the data available from literature on the thickness (D) variation of Curie temperature (T_C) and M_S of LSMO films grown under 200, 150, and 0.38 mTorr pressures of O_2 are analyzed in terms of the finite-size scaling, with M_S vs. D data fit to $M_S(D) = M_S(b)(1-d/D)$ yielding the dead layer thickness d = 1.1 nm, 1.4nm and 2.4 nm respectively.

Extending Additive Manufacturing to the Atomic Scale Focus Topic
Room 102B - Session AM+NS+SS-WeM
Nanofabrication with Focused Electron Beams (8:00-10:00 am)/Atomic Scale Manipulation with Focused Electron Beams (11:00 am-12:20 pm)

Moderator: Ondrej Dyckoe, Oak Ridge National Laboratory

8:00am **AM+NS+SS-WeM1 3D Nano-Printing via Focused Electron Beams: An Emerging Technology for Novel Applications***, **Harald Plank**, R. Winkler, J. Sattelkow,* Graz University of Technology, Austria*; J.D. Fowlkes,* Oak Ridge National Laboratory*; P.D. Rack,* University of Tennessee Knoxville **INVITED**

3D-printing of functional structures has emerged as an important technology in research and development. While being reliable on the micro and sub-micron scale, the extension to the nanoscale is still a challenging task. Among the very few direct-write techniques on that scale, focused electron beam induced deposition (FEBID) is one of the promising candidates as this technology allows fabrication of functional nano-structures on almost any material and substrate morphology in a single-step process. Based on strong fundamental progress in recent years, FEBID was demonstrated to be capable of fabricating complex, freestanding 3D nano-architectures with individual branch diameters down to 20 nm. Together with the increasing availability of precursors with different functionalities, FEBID is advancing from a versatile research tool into a predictable and reliable 3D nano-printer, which opens up new opportunities for advanced applications.

In this contribution, we start with the basic principles of 3-dimensional printing via FEBID, complemented by simulations for deeper insight into the fundamental processes that are operative. In the following, we present a variety of 3BID based proof-of-principle studies to demonstrate the capabilities of this direct-write technology. This ranges from scientifically oriented applications, such as plasmonics, magnetics and nano-mechanics toward industrially relevant concepts for scanning probe microscopy related tip fabrication, such as electrical, thermal and optical 3D nano-probes. Finally, we overview some of the remaining challenges and provide an outlook on future activities.

8:40am **AM+NS+SS-WeM3 3D Nanoprinting using an Electron Beam: Simulations and Computer-aided Design***, **Jason Fowlkes**,* Oak Ridge National Laboratory*; R. Winkler,* Graz Centre for Electron Microscopy, Austria*; B.B. Lewis,* Carl Zeiss Microscopy, LLC*; A. Fernandez-Pacheco, L. Skoric, D. Sanz-Hernandez,* University of Cambridge*; M.G. Stanford, E. Mutunga, P.D. Rack,* University of Tennessee*; H. Plank,* Graz University of Technology, Austria **INVITED**

The deposition of complex 3D nanoscale objects with prescribed geometry and function constitutes a major goal of nanoscience. Additive assembly is the ideal approach to efficiently deposit 3D materials. Focused electron beam induced deposition (FEBID) is a resist-free, direct–write method suitable for the additive deposition of materials on both planar and nonplanar surfaces. During FEBID, a focused electron beam is scanned along the substrate surface inducing the deposition and condensation of absorbed precursor molecules, often an organometallic, delivered locally by an in-situ gas injector. Until recently, 3D deposition using FEBID was mostly a trial-and-error exercise lacking a reliable framework to deposit a wide range of geometries.

A design environment specific to beam induced deposition will be presented that has enabled the deposition of complex, 3D nanoscale mesh style objects spanning nanometer to micrometer length scales. A complementary 3D simulation of FEBID provides a predictive capability that aides in the design of more complex 3D deposits. The purpose of this design/simulation capability is to generate the primary electron beam coordinates and beam exposure dwell times necessary for the experimental deposition of 3D mesh objects, with a reduced fill factor, i.e., geometries required for the design of metamaterials, high–aspect ratio sensors/actuators and/or nanomagnetic/optical lattices.

The simulation reveals that precursor surface diffusion and electron beam induced heating, in particular, can impose unwanted mesh object distortions if not properly accounted for. This general rule applies for several precursors under picoampere, millisecond beam exposure using typical local precursor fluxes consistent with high vacuum scanning electron microscope operation. Compensation for these influences can be applied in either the CAD phase, as geometric distortions, or through the introduction of exposure pulsing which acts to mitigate the development of transient mass/heat gradients. The role of simulation in design will also be explained in the context of the proximity effect due to scattered electrons, specifically their role in inducing unwanted deposition. Simulation results are limited to cases where complementary experiments converge with simulated predictions in terms of the final deposit geometry and the electrical current collected dynamically during deposition.

11:00am **AM+NS+SS-WeM10 Single Atom Scale Manipulation of Matter by Scanning Transmission Electron Microscopy***, **Stephen Jesse**, O. Dyckoe, S.V. Kalinin,* Oak Ridge National Laboratory **INVITED**

Fabrication of atomic scale structures remains the ultimate goal of nanotechnology. The reigning paradigms are scanning probe microscopy (SPM) and synthesis. SPM assembly dates to seminal experiments by Don Eigler, who demonstrated single atom manipulation. However, stability and throughput remain issues. The molecular machines approach harnesses the power synthetic chemistry to build individual functional blocks, yet strategies for structural assembly remain uncertain.

In this presentation, I discuss research activity towards a third paradigm — the use of the atomically focused beam of a scanning transmission electron microscope (STEM) to control and direct matter on atomic scales. Traditionally, STEM's are perceived only as imaging tools and beam induced modifications as undesirable beam damage. Our team and several groups worldwide have demonstrated that beam induced modifications can be more precise. We have demonstrated ordering of oxygen vacancies, single defect formation in 2D materials, and beam induced migration of single interstitials in diamond like lattices. What is remarkable is that these changes often involve one atom or small group of atoms, and can be monitored real-time with atomic resolution. This fulfills two out of three requirements for atomic fabrication. I will introduce several examples of beam-induced fabrication on the atomic level, and demonstrate how beam control, rapid image analytics, better insight through modelling, and image- and ptychography based feedback allows for controlling matter on atomic level.

This research is supported by and performed at the Center for Nanophase Materials Sciences, sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, BES DOE.

11:40am **AM+NS+SS-WeM12 Single Atom Modification of 2D Materials: Fabrication and Electronic Structure***, **Demie Kepaptsoglou**, F. Hage,* SuperSTEM Laboratory, UK*; T. Susi, J. Kotakoski, J. Meyer,* University of Vienna, Austria*; Y.C. Lin, K. Suenaga,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; T. Hardcastle,* University of Leeds, UK*; U. Bangert,* University of Limerick, Republic of Ireland*; JA. Amani, H. Hofsaess,* University of Göttingen, Germany*; Q. Ramasse,* SuperSTEM Laboratory, UK, United Kingdom of Great Britain and Northern Ireland **INVITED**

The past decade has seen incredible progress in the ability to isolate and manipulate two-dimensional crystals. Due to their unique structure and dimensionality, it is possible to confine charge carriers in two dimensions, resulting in peculiar physical, chemical and electronic properties. Such novel properties can be further controlled and tuned through defects such as single atom dopants, interfaces, etc. This defect engineering takes place quite literally at the atomic level, where a combination of low voltage scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS) and *ab-initio* calculations provides not only the most powerful means of characterization, but also a unique tool for manipulating the single atom structures and engineer their electronic interaction with the host matrix. This approach was recently used to demonstrate that low energy ion implantation (of dopants such as N and B) can be successfully implemented to introduce single substitutional defects with excellent retention rates and without affecting the structural integrity of the surrounding graphene matrix. Atomically-resolved EELS experimental data reveals the bonding signature of the dopants themselves and their impact on the surrounding lattice. *Ab initio* calculations, in excellent agreement with the experiment, confirm the nature of the excited states being probed by the EELS experiments and the electronic structure reconfiguration of the doped material around the single atom dopants. Results directly confirm the possibility of tailoring the plasmonic properties of graphene in the ultraviolet waveband at the atomic scale, a crucial step in the quest for utilizing it's properties toward the development of plasmonic and optoelectronic devices. The gentle STEM observation conditions can also be used to controllably drive the diffusion of substitutional dopants through single layer graphene, one atomic jump at a time. Atomically precise manipulation with STEM relies on recent advances in instrumentation that have improved the instruments' stability and their beam positioning abilities. While momentum transfer from highly energetic electrons often leads to atom ejection, interesting dynamics can be induced when the transferable kinetic energies are comparable to bond strengths in the material. For instance, a combined experimental and theoretical study revealed that for Si dopants manipulated in the STEM by 60keV electrons these jumps are not due to impacts on the Si atom, but to sub-threshold impact events on the surrounding C atoms. This approach suggests that STEM could emerge as an alternative method for the direct assembly of nanostructures.

Applied Surface Science Division
Room 204 - Session AS+NS+SA-WeM

Beyond Traditional Surface Analysis

Moderators: Mark Engelhard, Pacific Northwest National Laboratory, Kathryn Lloyd, DuPont Corporate Center for Analytical Sciences

8:00am **AS+NS+SA-WeM1 Solar Wind Interaction with Carbonate Deposits on Asteroid (1) Ceres' Surface: The Role of Surface Analysis in Laboratory Planetary Science***, **Catherine Dukes**, G. Rodriguez Lopez, C. Bu,* University of Virginia

Bright deposits of anhydrous carbonates across the dark background of dwarf-planet Ceres have been identified by Dawn's VIR spectrometer with a composition that varies from natrite with minor amounts of ammonium bicarbonate within the Cerealia and Vinalia Faculae to magnesite, calcite, and dolomite in other high-albedo regions [1]. These deposits are expected to derive from the aqueous alteration of volatile-containing silicates, forming a viscous brine below Ceres' solid crust. Hydrated salts from this reservoir are deposited on the planetary surface by extrusion through vents or co-ejected by jets of sub-surface water ice. Water loss in the material occurs with exposure to the low pressure environment on Ceres' surface as a function of exposure time, even at temperatures < 240 K [2].

Unprotected from the impacts of solar particles, cosmic rays, and meteorites, anhydrous salts undergo chemical and physical change (space weathering), which can be remotely identified by optical reflectance. The effect of solar-wind ions on carbonates can be simulated in the laboratory, and the correlation between surface composition and morphology with optical change can be used to infer physical processes occurring on airless planetary bodies. We investigate the stability of carbonates and measure systematic darkening with 4 keV He-ion fluence, a potential geologic chronometer for Ceres' bright deposits.

Carbonate powders are pressed into pellets, then introduced into vacuum (10^{-9} Torr) and cooled to ~110/200 K.

An external-beam from an FT-IR is used to perform *in-vacuo* reflectance measurement. Spectra were acquired at varied fluence, equivalent to solar irradiation of ~300 - 30,000 years at 2.8 A.U. Changes in surface composition and molecular chemistry were investigated by *in-situ* X-ray photoelectron spectroscopy (XPS).

Blueish luminescence of sodium carbonates with He^+ is observed. Vis-NIR darkening (~80%) of natrite (Na_2CO_3)occurs after 10^{18} He cm^{-2}, with reddening of the visible spectral slope. Similar darkening is noted for 1.3 - 5 µm, along with attenuation of carbonate overtones. Concomitant XPS measurement shows a reduction of carbon and oxygen, with enhancement of sodium. Exposure of the darkened sample to 10,000 L H_2O-vapor results in brightening to > 80%.

Ion-induced darkening of Ceres' natrite deposits is expected to occur on a time-scale of 100 - 1000 years, and can be reversed by exposure to water vapor. For deposits of varied albedo, this suggests that the brightest areas are the most recent deposits or the most recently exposed to water.

[1] DeSantis et al. (2016) Nature 536, 54-57

[2] Bu et al. (2017) Icarus doi.org/10.1016/j.icarus.2017.12.036

8:20am **AS+NS+SA-WeM2 Looking Deeper and Smaller: Enhancing XPS by Hard X-ray Probes and High-resolution Imaging*, Olivier Renault,*** CEA/LETI-University Grenoble Alpes, France*; C. Zborowski,* University of Southern Denmark*; J.-P. Rueff,* Synchrotron SOLEIL, L'orme des Merisiers, France*; Y. Yamashita, S. Ueda,* NIMS, Japan*; G.A. Grenet,* Lyon Institute of Nanotechnology, France*; S. Tougaard,* University of Southern Denmark

X-ray photoelectron spectroscopy (XPS) has become a mature technique with a widespread use spanning from fundamental research to R&D labs. In parallel, the intrinsic complexity of materials and systems to be analyzed by XPS has increased. Some of the limitation of XPS are of concern if a non-destructive, non-invasive analytical protocol is the key issue. These are, especially, the poor lateral resolution and the poor bulk sensitivity, making impossible the analysis of microscopic features and buried interfaces in a reliable way.

In this contribution, we review the capabilities of current and novel techniques to get into: (i) high lateral resolution and quantitative micro-analysis using spectroscopic imaging implemented by X-ray PhotoElectron Emission Microscopy (XPEEM); (ii) high depth sensitivity offered by Hard X-ray Photoelectron Spectroscopy (HAXPES), coupled or not with inelastic background analysis to futher enhance information depth up to nearly 100 nm.

We will highlight the capabilities of each techniques by different practical examples in the field of 2D materials [1] and device technology [2, 3], emphasizing particularly the perspectives offered by novel laboratory hard X-ray sources [4].

[1] H. Kim, O. Renault et al., Physical Review B, 2016. 94(8): p. 081401.

[2] P. Risterucci, O. Renault et al., Applied Surface Science, 2017, 402: p. 78-85.

[3] C. Zborowski, et al., Applied Surface Science, 2018. 432(Part A): p. 60-70.

[4] O. Renault, E. Martinez, et al., Surf. Interface Anal. 2018 (in press).

8:40am **AS+NS+SA-WeM3 Reenvisioning Amphiphilicity: Translating Cell Membrane Design Principles to Synthetic 2D Materials*, Shelley Claridge,*** Purdue University **INVITED**

2D materials such as graphene exhibit unique electronic and mechanical properties that promise substantial advantages in applications ranging from nanoelectronics to human health. Such interfaces are often functionalized noncovalently with lying-down phases of functional molecules to avoid disrupting electronic structure within the basal plane. Interfacial structures have commonly been characterized down to sub-nm scales using scanning probe techniques such as STM, either in vacuum, or at a solid-liquid interface with a nonpolar liquid (e.g. octadecene). However, molecules used in this approach are often structurally similar to amphiphiles such as fatty acids and phospholipids found in biological cell membranes, suggesting possible utility in *aqueous* environments. At the same time, the overall surface chemistry is strikingly different than that of the cell membrane -- in essence, the surface chemistry is that of a repeating cross-section of a lipid bilayer, with both hydrophilic and hydrophobic components exposed, forming a striped amphiphilic structure with sub-10-nm periodicity.

As 2D materials are integrated into hybrid materials and devices, this noncovalent amphiphilic interfacial structure raises two classes of significant questions requiring interfacial analysis: ***(1) How do noncovalent lying-down ligand layers respond to solution or thermal processing?*** What are the best ways to probe controlled *disordering* across scales from nm to mm at an interface with a polar liquid? If ligand dynamics vary with structure, to what extent can design principles from the cell membrane be invoked to control chemical functionality and reactions at the interface? ***(2) Can noncovalently-adsorbed layers be patterned to template further interactions with the environment?*** Lying-down phases of phospholipids and fatty acids present 1-nm-wide stripes of ordered chemical functional groups, suggesting the possibility of controlling processes such as crystallization, phase segregation, or analyte binding. We examine these questions, again developing approaches to characterize interface structure across the range of relevant length scales, and invoking structural design principles from the cell membrane.

9:20am **AS+NS+SA-WeM5 Microstructural Effects on Surface Potential of Amorphous Solid Water*, Caixia Bu,*** *C.A. Dukes,* University of Virginia

Amorphous solid water (ASW) formed by vapor deposition on substrates <~130 K is of interest for its abundance in Earth's upper atmosphere, icy planetary bodies, and throughout the interstellar medium, as well as its use as model material in many disciplines. Two crucial characteristics of ASW are a self-induced negative surface potential and formation of nanopores [1]. Here, we examine the role of microstructure, including nanopores, on the spontaneous surface potential of ASW, and describe the complementary experimental techniques used, which have application for other microporous solids.

ASW films were deposited by directed vapor beams onto a He-cooled quartz-crystal microbalance (QCM) under ultra-high vacuum. The integrated pore volume (porosity) was calculated by combining the areal mass measured via QCM and thickness measured by UV-visible interferometry. The integrated surface area was indicative by the abundance of incompletely coordinated surface water molecules (H_2O) on the pores, using the O-H dangling bonds (DBs) measured by FT-IR spectroscopy. An *in-situ* Kelvin probe measured film surface potential. A long-distance optical microscope monitored film morphology *in vacuo*. Annealing effects were investigated by heating the film at 1.8 K/min.

The magnitude of the negative surface potential ($|V_s|$) increased linearly with film thickness at rates ($|\Delta V_s/\Delta L|$) that decreased with increasing growth temperature (T_g = 10–110 K), keeping deposition angle at $\theta = 0°$ (angle between vapor beam and QCM normal); at T_g = 30 K, the $|\Delta V_s/\Delta L|$ decreased with increasing θ (= 10−75°). ASW porosity showed no dependence on T_g at $\theta = 0°$, but increased significantly with increasing θ. The H_2O DBs decreased/increased with increasing T_g/θ, showing similar trends as the $|\Delta V_s/\Delta L|$. Upon heating, the most striking result was that the DB at ~3720 cm^{-1} (from two-coordinated H_2O) and the $|V_s|$ had similar temperature-dependent evolutions. By correlating all measurements, we propose that the observed intrinsic ASW surface potential results from aligned incompletely-coordinated H_2O on the pore surfaces [2].

The $|V_s|$ decreased abruptly when ASW thickness exceeded a critical value (L_c), and cracks appeared in the optical images of the films. The L_c, ~1−5 µm (T_g = 10–50 K; θ = 0–55°), increased with T_g and θ, suggesting dependences on the microporous structure. We explain such dependences of L_c in the context of Griffith theory and estimate the tensile strength of ASW to be ~25–40 MPa [3].

We acknowledge support from the NASA LASER Program.

[1]Raut et al., *J. Chem. Phys.***127**, 204713 (2007); [2]Bu et al., *J. Chem. Phys.***143**, 074702 (2015); [3]Bu et al., *Appl. Phys. Lett.***109**, 201902 (2016).

9:40am **AS+NS+SA-WeM6 Speciation and Reactivity of Organic Matter in Uranium Mine Wastes from Laguna- New Mexico: An Application of Surface Sciences in Environmental Systems.*, Carmen A. Velasco,*** *A.M. Ali,* University of New Mexico*; C. Osburn,* North Carolina State University*; K. Artyushkova, J.M. Cerrato,* University of New Mexico

The co-occurrence of organic matter and uranium in the Jackpile Morrison formation, New Mexico was investigated using spectroscopy, microscopy, and water chemistry techniques to better understand the effects of organic matter on uranium (U) binding from abandoned U mine wastes. Samples were collected from the Jackpile Mine (JP)- New Mexico. The mean concentration of acid extractable content for mine waste from the JP was 2.61±0.09% U. Results from microprobe mapping suggest that U particles are surrounded by carbon (C) inclusions, while results from XRF analyses showed 2.78% (JP) carbon (C). Loss on ignition (LOI) analysis showed that 19.90±0.95% of organic carbon within the samples. Thermal gravimetric analysis (TGA) show the maximum weight loss between 105°C and 505°C, confirming that change on mass after the LOI is likely due to the loss of organic content of the samples. Analyses using XPS suggest that changes occur on the C binding and U oxidation state after modifying the pH in batch experiments. Emission Matrix (EMM) identified humic-acid and fulvic-acid like components present in the organic matter comprised in the mine waste, which is consistent with the organic functional groups detected by XPS. These findings suggest that uranium minerals are possibly complexed carboxylic functional groups from humic-and fulvic like substances. This study identified the relevance of considering the binding of U and C in mine wastes to better understand U mobilization in the environment.

*This work was awarded the best talk award at the 2018 NMAVS Symposium (Albuquerque-May2018)

11:00am **AS+NS+SA-WeM10 Optical Constants Measured for Iridium and Samarium by Reflection Electron Energy-loss Spectroscopy Spectra***, **LiHao Yang**, H. Xu,* University of Science and Technology of China*; A. Sulyok, M. Menyhard,* Institute for Technical Physics and Materials Science Centre for Energy Research, Hungarian Academy of Sciences (MTA)*; K. Tokesi,* Institute for Nuclear Research, Hungarian Academy of Sciences (ATOMKI)*; Z.J. Ding,* University of Science and Technology of China

The optical properties, as one of the most important physical properties of materials, arouse a continuous interest of researchers. Accurate measurement of optical data by optical methods in a photon energy range up to 100 eV is still insufficient as special experimental conditions are required during the measurements in vacuum ultraviolet region (20-50 eV). In recent years a well-established technique based on the reflection electron energy loss spectroscopy (REELS) has been developed to obtain optical constants in a rather wide range of electron energy loss. The REELS method does not require a complicated process for preparation of samples and the incident electron energy is usually around a few keV. However, the REELS spectrum usually contains not only bulk excitation but also surface excitation. To remove the surface excitation effect from the REELS spectrum in data analysis, Da et al. [1] have developed a reverse Monte Carlo (RMC) method for the derivation of the energy loss function (ELF) which is directly related to optical constants of a solid.

In the present work, reflection electron energy loss spectra of Ir and Sm were measured at several primary energies ranging from 0.5 keV up to 2 keV and in a wide energy-loss range. Polycrystalline Ir and Sm samples were cleaned by Ar+ ion bombardment. To minimize the surface roughening and damage, glancing incidence angle of 80° with respect the surface normal and low projectile energy of 1 keV were applied with the rotated sample during the sputtering. Cleanliness of surface was checked by continuous detection of main Auger peaks of C and O. A reverse Monte Carlo simulation was performed to extract ELFs of these metals from experimental REELS spectra. All the ELFs have produced REELS spectra in a good agreement within the experimental uncertainty. The reliability of the obtained optical data has been confirmed by applying the Thomas-Ritchie-Kuhn (f-sum rule) and the perfect-screening sum rules (p-sum rule). The good agreement indicates that RMC treats accurately the surface excitation effect which is well removed from the final ELF. Comparisons of our data with other sources from experimental measurements are given.

The work was support by the National Natural Science Foundation of China (No. 11574289) and Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (2nd phase) under Grant No. U1501501.

Reference:

[1] B. Da, Y. Sun, S. F. Mao, Z. M. Zhang, H. Jin, H. Yoshikawa, S. Tanuma, and Z. J. Ding, J. Appl. Phys. 113, 214303 (2013).

11:20am **AS+NS+SA-WeM11 X-Ray Photoelectron Spectroscopy and Electrical Modeling of Electrowetting on Dielectric Devices***, **Pinar Aydogan Gokturk**,* Bikent University, Turkey*; B. Ulgut, S. Suzer,* Bilkent University, Turkey

Electrowetting on dielectrics (EWOD) is a process of changing the contact angle of a droplet sitting on the dielectric covered electrode by the application of external electric field. In majority of the electrowetting experiments reported in the literature, water or aqueous salt solutions are used and ambient medium is either the air, or another immiscible liquid like oil. In this study, for the first time two non-aqueous liquids; (i) polyethylene glycol with an average molecular weight of 600 Da, and (ii) DEME-TFSI ionic liquid, both with low vapor pressure and volatility, are used as droplets in the UHV chamber of an x-ray photoelectron spectrometer (XPS) with traditional electrowetting on dielectric device geometry. With the experimental determination on tracing the electrical potential developments on and around the droplet, using the shifts in the binding energy positions of peaks coming from the liquid and/or the substrate, under imposed AC and DC electrical fields, we are aiming to shed light on the numerous models employed for simulating the electrowetting phenomenon. Additionally, using XPS and incorporating real capacitors and resistors, we mimic and check on the commonly used models used for simulating the electrical behavior of the EWOD systems. Possible and accepted electrical circuit models are also used to simulate the XPS data.

11:40am **AS+NS+SA-WeM12 Near Ambient Pressure XPS Study of Oxygen Binding to the Surface of Transition Metal-nitrogen-carbon Electrocatalysts for Oxygen Reduction***, K. Artyushkova, **Yechuan Chen**, P. Atanassov,* University of New Mexico

The most promising class of platinum group metal-free materials for oxygen reduction reaction (ORR) is based on graphene-like carbon containing nitrogen and transition metal (MNC). It is well established that nitrogen coordination with metal in the carbon network of MNC materials is directly related to ORR activity; however, the exact nature of the active sites is still debated even after over 50 years of research.

The mechanism of oxygen reduction reaction in metal-nitrogen-carbon (MNC) catalysts has been studied by a combination of spectroscopic and theoretical structure-to-activity studies. Using inhibitors that have unique spectral signatures and have strong binding to the active sites allows elucidating the relationship between the chemistry of active sites and its activity.

We will report laboratory-based and near ambient pressure (NAP-XPS) analysis for series of electrocatalysts belonging to Fe-N-carbon families. X-ray photoelectron spectroscopic analysis of the interaction of complexing agents based on phosphonate and *in situ* monitoring of oxygen binding to metal-free active sites provides an important insight into the reaction mechanism. The effect the nitrogen chemistry and the type of iron on the oxygen binding was investigated by NAPXPS under an oxygen environment at operating temperature of the fuel cell. Preferential oxygen binding to different types of nitrogen and iron moieties in presence and absence of inhibitor was followed by spectroscopic changes in high-resolution nitrogen photopeak.

12:00pm **AS+NS+SA-WeM13 Surface Chemistry of Scandium***, **Michael Brumbach**, D.A. Casalnuovo, E.V. Barnat, C. Winters, D. Robinson Brown, C.S. Snow, A.M. Grillet,* Sandia National Laboratories

Manipulation of metal surface chemistry through vacuum gas dosing has been demonstrated for many years. Additionally, ex situ preparation methods, ion sputtering, and/or in vacuo thermal treatment are all known to change surface properties through oxidation, removal of oxide, change in microstructure, altering contaminants, or other mechanisms. While these studies have been performed for decades, there are few examples of these experiments for pure scandium films. Furthermore, few examples of dosing clean scandium surfaces under vacuum have been published. In this work, scandium films were treated with UV/ozone ex situ cleaning, ion sputtering, and thermal treatment under UHV. These surfaces were then exposed to different gases in the millitorr pressure range for extended periods of time. An optical emission spectrometer was used to monitor the composition of the dosing gas. Surfaces were analyzed before and after dosing. In concert with the gas analyses, the changes in surface chemistry of scandium could be correlated to the dosing species. This work discusses the X-ray photoelectron peak fitting of scandium and the changes in chemistry that can be observed through surface exposures.

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Electronic Materials and Photonics Division
Room 101A - Session EM+AN+MI+SS-WeM

Surface and Interface Challenges in Electronics and Photonics

Moderators: Andy Antonelli, Nanometrics, Michael Filler, Georgia Institute of Technology

8:00am **EM+AN+MI+SS-WeM1 Few Monolayer Atomic Layer Deposition (ALD) to Engineer New Surfaces and Interfaces***, **Parag Banerjee**,* Washington University in St. Louis **INVITED**

Atomically precise modification of surfaces and interfaces with few monolayer material leads to improved understanding and significant enhancements in properties, performance and reliability of heterogeneous materials and devices. This talk highlights the impact of few monolayer insulators, wide bandgap semiconductors and metals, deposited using atomic layer deposition (ALD) on a variety of surfaces and interfaces with direct relevance to electronic and photonic devices.

The first part of this talk deep dives into the process science of ALD in its early cycles. The nature and structure of few monolayer ALD films is highlighted. In particular, configurational state and entropy of adlayers during every half-cycle of ALD[1] is exploited to exquisitely manipulate nucleation and growth of metallic Ru thin films.[2]

In the second part of this talk, applied aspects of few monolayer engineering of surfaces and interfaces is discussed. Case studies included are the non-linear optical phenomena on $Au-Al_2O_3$ and Au-ZnO surfaces,[3] high performance photocatalysts for CO_2 photoreduction,[4] improved optoelectronic responses from surface passivated CuO nanowires[5] and few monolayer Ta_2O_5 to improve reliability of electrochromic windows.[6]

Regardless of the application, ALD at its ultimate thickness limit holds true potential for surface and interface engineering. The control of this process appears to be remarkably simple and yet, has hidden complexities that continue to push the boundaries of discovery of new materials and concept devices.

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8:40am **EM+AN+MI+SS-WeM3 Lattice-alignment mechanism of SiGe on Sapphire*, HyunJung Kim,*** National Institute of Aerospace*; S. Choi,* NASA Langley Research Center

In the conventional heteroepitaxy processes, the deposition of dissimilar materials has been made with the same or similar crystal structure and perfect or nearly matching lattice constants, such as Ge/Si (diamond cubic), InAs/GaAs (zinc-blende), and GaN/Al_2O_3 (hexagonal/trigonal). On the other hand, the super-heteroepitaxy of two semiconductors with dissimilar crystal structures such as SiGe (diamond cubic)/Al_2O_3 (trigonal) is not readily achievable but requires scrupulous manipulation of growth conditions for single crystal formation. Epitaxial growth patterns of SiGe on *r*-plane and *c*-plane of sapphire substrates show 90^o-rotated and 60^o-rotated twin defects, respectively [1,2].

A team at NASA Langley Research Center developed a technique for super-hetero-epitaxy of single crystal SiGe growth; diamond-cubic structure of SiGe on trigonal structure of the *c*-plane sapphire substrate by a transformed lattice structure under a new lattice-alignment model [2]. Although the growth conditions were effective for the formation of single crystal film, how the mechanism or physics of single crystal formation of SiGe at the interface of sapphire was not theoretically and experimentally defined with the order of atomic scale level in arrangement. This work presents the interfacial image of $SiGe/Al_2O_3$ using high-resolution transmission electron microscope (HRTEM) to show the $SiGe/Al_2O_3$ interfacial bonding for superheteroepitaxy mechanism. The first two atomic layers of the SiGe are Si-rich where Si atoms match with the surface oxygen lattice of the Al_2O_3 substrate. After the Ge composition increases, the monolayer spacing is also increased due largely to the dominance of Ge composition since the lattice constant of Ge is bigger than that of Si. These results highlight the importance of a cleanliness of sapphire substrate, the Si-affinity to oxygen that ties up Si- of SiGe with the oxygen of sapphire, and eventually causing the deformation of SiGe cubic structure for super-heteroepitaxy [3]. From the essential understanding of the $SiGe/Al_2O_3$ interface mechanism, both low temperature SiGe super-heteroepitaxy and the III-V or II-VI semiconductor epitaxy are possible.

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9:00am **EM+AN+MI+SS-WeM4 An Effort to Resolve Band Offset Anomalies in ZnO/GaN Heterostructures*, Monu Mishra*[1]***, A. Gundimeda, V. Vandana, G. Gupta,* CSIR-National Physical Laboratory, India

Gallium Nitride (GaN) and Zinc Oxide (ZnO) are well established wide band gap (WBG) semiconductors facilitating potential application in futuristic energy-efficient opto/micro-electronics technology. Despite of owing the merits of both semiconductors, the understanding of ZnO/GaN heterostructures is still posing challenges. The available reports display anomalies amongst calculated valence band offset (VBO) and defect state of ZnO/GaN interface. The influence of surface and interfacial properties perturbs the electronic structure, localized charge density and defect states at the interface, yet the impact of these properties on VBO requires more scientific attention. Hence, sharp interfaces of ZnO/GaN heterostructures (ZnO thickness = 2, 5 and 8 nm) were fabricated via atomic layer deposition (ALD) of ZnO on MOCVD grown highly crystalline GaN epilayer and further investigated by HR-XPS, UPS and PL spectroscopy. The impact of ZnO thickness on band bending (upwards & downwards), surface/interface dipole strength and defects states (vacancies, interstitials, donor/acceptors etc.) on valence & conduction band offsets (VBO/CBO) were thoroughly analysed. It was observed that the VBO at the interface was reduced via 0.6 eV as the ZnO thickness was increased from 2 nm to 8 nm which was ascribed to interface dipole strength along with dramatic change in localized BB (downwards-flatband-upwards). A type-II band alignment was perceived at all ZnO/GaN interfaces though the nature & contribution of defects states (especially oxygen vacancies and zinc interstitials) varied incommensurately. The defect band spectra revealed a blue shift (~502 eV) which correspond to the conversion of yellow-green emission in ultrathin ZnO/GaN heterostructure (2 nm ZnO) to characteristic green emission in bulk ZnO. The analysis revealed that the thickness of ZnO overlayer in ZnO/GaN heterostructure significantly alters the electronic structure and defect states at the interface and thus the resolution of anomalies in the present analysis would be useful for the fabrication of ZnO/GaN heterostructure based efficient optoelectronic devices.

9:20am **EM+AN+MI+SS-WeM5 Stress Relaxation in the Si-SiO2 System and its Influence on the Interface Properties*, Daniel Kropman,*** *T. Laas,* Tallinn University, Estonia*; A. Medvids,* Riga Technical University, Latvia

It is known that internal mechanical stresses (IMS) due to the differences in the thermal expansion coefficients between films and substrates and lattice mismatch appear in the Si-SiO_2 system during the process of its formation and that point defects (PD) generation and redistribution could be used to reduce partially the surface stress. However, this process on the atomic scale is till not studied. The goal of the present report is to investigate the stress relaxation mechanism in the Si-SiO_2 system using EPR, IR absorption spectroscopy, scanning elektron microscopy (SEM) and samples deflection measurements. PD density and stresses in the Si-SiO_2 system were varied by oxidation condition (temperature, time, cooling rate, ambient) and by Si_3N_4 deposition on SiO_2. Different sign of the thermal expansion coefficient of the SiO_2 and Si_3N_4 on Si allow to modifay the IMS at the interface. It has been found that samples deflection decreases or increases simultaneously with EPR signal intensity depending on the oxidation condition (temperature).

At oxidation temperature 1100^0C the deflection of the samples(h) decreases with the increase of EPR signal intensity (vacancies),while at a oxidation temperature 1200^0C EPR signal (I) and deflection increase simultaneously. Those allows to suggest that at lower oxidation temperature PD (vacancies) reduce the tensil IMS in Si, while at higher oxidation temperature compressive IMS created PD in SiO_2 (E' centers).At an intermediate oxidation temperature tensil stresses in Si and compressive stresses in SiO_2 may bee equal and compensate each others. It has been find that at oxidation temperature 1130^0C IMS at the Si-SiO_2. interface are lower than at 1100^0C and 1200^0C. Lower defect dencity on samples crossection microphotos obtained by SEM and PD dencity diminishing.in samples oxidized at 1130^0C confirmed thise suggestion.In Fig,2 the EPR signal and IR absorbtion line-width dependence on the oxidation time is shown. It can bee seen ,that EPR signal and IR absorbtion line-width at 1100 cm^{-1} dependence on the oxidation time (oxide thickness) is nonmonotonous and depended on the cooling rate .In slowly cooled samples the increase of the EPR signal is accompanied by the decrease of Δν but,in fast cooled samples EPR signal and Δν increase simultaneously with increase oxidation time.

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[1] **National Student Award Finalist**

Absent of the cooling rate influence on the PD density and Δν dependence on the oxidation time at I(t) and Δν(t) dependence intersection points show, that IMS by an appropriate choice of the SiO_2 film thickness dissapear.

9:40am **EM+AN+MI+SS-WeM6 Unique Sensitivity to Deep Trap States Demonstrated by CREM of Broad Bandgap Dielectric Layers***, **Hagai Cohen,*** Weizmann Institute of Science, Israel*; K.X. Steirer,* Colorado School of Mines

Chemically resolved electrical measurements (CREM) present an efficient and sensitive means for studies of structural-electrical inter-relationships in heterostructures. Operated in-situ to x-ray photoelectron spectroscopy (XPS), the technique is yet far from being fully exploited. Recent progress in our CREM instrumentation has, however, opened new opportunities to which this report is dedicated. Using broad-bandgap dielectric layers, such as SiO_2, SiON and ZnOS, we tested the CREM resolving power and sensitivity to charge trap states. These experiments yielded band diagrams with fine details on charge traps, which typically require the application of advanced optical techniques combined with the electrical characterization tools.

In addition, an intriguing process of doubly triggered conductance in ZnOS was observed. The ZnOS layers exhibited very poor conductance under either electrical or optical input signals, whereas simultaneous application of the two yielded extremely high sample currents. Based on the in-situ derived band diagram, a comprehensive explanation of the effect is provided. Moreover, we show how the CREM analytical tool can also provide a potential activator of future related devices.

11:00am **EM+AN+MI+SS-WeM10 Fabrication of Multilayered Optically Active Nanocrystal Solids by Surface Passivation using Metal Oxides: ALD vs CVD***, **Riya Bose**, A.D. Dangerfield,* University of Texas at Dallas*; S.M. Rupich,* University of Texas*; Y.J. Chabal, A.V. Malko,* University of Texas at Dallas

Semiconductor nanocrystal quantum dots (NQDs) provide a powerful platform for optoelectronic applications with their size/shape/composition tunable properties and inexpensive solution based synthesis techniques. Integration into solid state devices requires deposition of NQD films, and often a controlled assembly of multilayered NQD structures to ensure maximum light absorption and optimum efficiency of the devices. However, thin film fabrication is found to degrade its properties compared to NQDs in solution, especially a decrease in the photoluminescence (PL) quantum yield (QY) is frequently observed. Also, the bottleneck for fabrication of multilayer NQD films remains the use of solution phase deposition methods, where the solvent in the subsequent step of deposition dissolves the initial layer until each NQD layer is rendered insoluble by means of any surface passivation technique. Surface passivation techniques also play a critical role to protect the deposited layers from oxidation and deterioration. An attractive method to passivate NQD films during the deposition as well as from environmental exposure is to overcoat them with various metal oxides grown using atomic layer deposition (ALD). Though there are few reports of ALD encapsulation of NQD films, they mostly attend to charge transfer-based devices and aim to improve carrier moblities. Typically, such studies report a significant quenching of the PL intensity after encapsulation. In this study, we aim to investigate the exact growth mechanism of metal oxide layers by ALD on the surface of NQD films and how it, along with the ALD parameters, affects their PL properties. With the aid of in-situ FTIR and ex-situ XPS measurements during Al_2O_3 deposition on oleic acid capped CdSe-ZnS core-shell nanocrystals, it is observed that the interaction of the metal precursor trimethyl aluminium (TMA) with the surface of the NQDs leads to the reorganization of the ligands as well as replaces Zn, leading to PL intensity quenching. In order to prevent this, we opted for a pulsed chemical vapour deposition (CVD) like approach for metal oxide deposition where simultaneous purging of both the metal and oxygen precursors leads to formation of metal oxide in a gas phase in the immediate vicinity of the NQD surface. We found that minimization of TMA interaction with the NQDs' surface indeed leads to enhancement of the PL intensity and elongation of carrier PL lifetime. These measurements provide clear indication of defect-free surface passivation proving that CVD-like Al_2O_3 encapsulation is a suitable technique for controlled deposition of multilayered NQD structures that preserves its optoelectronic properties.

11:20am **EM+AN+MI+SS-WeM11 The Role of Surface Oxides for the Optoelectronic Performance of III-V Semiconductor Nanowires***, J. Colvin, 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 [1,2], mainly due to their flexibility in creating heterostructures by axial stacking during epitaxial growth. Because of their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly determined by surface properties. We have previously studied surfaces and surface oxides of semiconductor NWs by scanning tunneling microscopy and spectroscopy (STM/S) [3] as well as X-ray photoemission spectroscopy [4]. Here, we will correlate the surface properties of InAs and InP NW heterostructures with their electrical and photovoltaic behavior, which has been measured for individual upright-standing NWs using the STM tip as local nanoprobe [5].

InP and GaInP pin-junction NWs have been cleaned from their native oxide by annealing under atomic hydrogen background and re-oxidized by exposure to ambient conditions. By illuminating the InP NWs that were contacted by the STM nanoprobe, we observed a decrease of the open-circuit voltage from 0.75 V to 0.70 V upon native oxide removal and an increase back to 0.76 V upon re-oxidation, confirming the need of surface passivation for improving InP solar cells. However, the ideality factor of the NW pin-diodes remained constant at n = 1.82 upon oxide removal, but improved to n = 1.67 upon re-oxidation. Furthermore, our XPS results indicate the outdiffusion of Zn dopants from the p-doped NW segments, forming a Zn-rich shell around the NW.

A more significant effect of the presence of native surface oxide was found for InAs NWs which consist of one segment of wurtzite and one segment of zincblende crystal structure. Upon removal of the native surface oxide, we obtained an increase in conductivity of these NWs by two orders of magnitude, while reference NWs with pure wurtzite structure showed a slight decrease in conductivity with the same surface treatment. This effect can be explained by a staggered type-II surface band alignment at the wurtzite/zincblende interface of oxidized NWs, which turned into flat-band conditions upon oxide removal, as confirmed by nano-focus XPS measurements.

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

[5] R. Timm *et al.,* Nano Lett. **13**, 5182 (2013).

11:40am **EM+AN+MI+SS-WeM12 Photonic Annealing of 2D Transition Metal Dichalcogenides for Tailored Optical Properties***, **Rachel Rai**, K. Gliebe,* University of Dayton; Air Force Research Laboratory*; N.R. Glavin, R. Kim, A. Jawaid, R. Wheeler, L. Bissell,* Air Force Research Laboratory*; C. Muratore,* University of Dayton

Thin layers of transition metal dichalcogenides (TMD) have attracted significant interest in the field of optoelectronics due to their unique light absorption and emission properties in the visible frequency range. Development of bright, flexible, large area emission sources based on 2D materials using photonic annealing represents an exciting opportunity for future quantum systems. Here we introduce new correlations relating the optical properties of WSe_2, a well-known single photon emitter, to post-processing annealing techniques to include lasers, broadband radiation, and nanoscale electron beams. Modulation of the total energy flux during growth of amorphous TMD material to develop purely amorphous materials or materials with nanoscale nuclei was employed by the authors to examine effects of pre-existing nuclei on crystallization kinetics (i.e., activation energy) and the resulting optical properties. We correlate the wavelength and intensity of photoluminescence from WSe_2 deposited on plasma treated and as-received flexible substrates and present techniques to control film continuity and the areal density of free edges from islands on discontinuous films for tuning the intensity of optical emission. A significant increase in photoluminescence intensity is accompanied by a change in domain boundary density, correlating well to theory. Furthermore, examination of quantum confinement effects by producing nanoscale crystalline areas (between 5-50 nm) with precisely controlled volumes via electron beam radiation provides insight on light emission mechanisms.

12:00pm **EM+AN+MI+SS-WeM13 Polarity Control of GaN Nanowires on Diamond: Experiment and Theory***, **Karin Larsson**,* Uppsala University, Sweden*; M. Hetzl, M. Kraut, T. Hoffmann, M. Stutzmann,* Technical University Munich, Germany

III-nitride nanowires on diamond substrates are of current interest for two different potential applications: (i) selectively grown n-type AlGaN nanowires on p/i – diamond are promising for the electrical control and the efficient optical and electrical readout of individual NV-centers in diamond as qubits and (ii) AlGaN/diamond n/p-heterodiodes are an interesting option for future ultraviolet LEDs and laser diodes. For both applications, the polarity of AlGaN nanowires grown on diamond has a strong influence on the optoelectronic properties of the heterojunctions, because the polarization-induced interface charge strongly influences the details of the diamond/III-nitride band alignment. Thus, the growth of nanowire arrays with randomly fluctuating polarity will have a negative influence on the electronic properties of the heterojunctions.

In this presentation, we will discuss recent experimental results concerning the control of GaN nanowire polarity on diamond (111) substrates via different surface termination treatments (hydrogenation, oxygen termination, nitrogen radical exposure [1]). Systematic experimental investigations have shown that even very well ordered periodic nanowire arrays deposited by Selective Area Growth exhibit a high degree of polarity disorder. Diamond is a well-suited substrate for these investigations, since it supports several different types of stable surface structures which only differ by about one monolayer and have a strong influence on the preferred nanowire polarity. The effect of different surface terminations on nanowire polarity will be recapitulated. Furthermore, we complement these experimental investigations by theoretically studying the effect of diamond surface termination on the energetically preferred GaN polarity. First principle DFT-calculations are used to calculate the interface energies and the corresponding atomic configurations of the different diamond/GaN interfaces. Strong variations observed in the interface chemistry between diamond and GaN nanowires will be discussed based on the available experimental and simulation data.

[1] M. Hetzl et al., Nano Lett. 17, 3582 (2017)

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 201A - Session HC+SS-WeM
Mechanisms and Reaction Pathways of Heterogeneously Catalyzed Reactions

Moderator: Johan Gustafson, Lund University

8:00am **HC+SS-WeM1 Surface Reactions of Methanol on Fe_3O_4(001) and Pd/Fe_3O_4(001) Model Catalysts***, **Matthew Marcinkowski**, N. Doudin, R.S. Smith, B.D. Kay, Z. Dohnalek,* Pacific Northwest National Laboratory

Single atom catalysts offer potential improvements in reactivity, selectivity, and decreased catalyst cost, but are often difficult to characterize and stabilize. Iron oxides are frequently used as catalyst supports, and recent studies have shown that Fe_3O_4(001) magnetite can stabilize isolated atoms of many transition metals.[1] This property makes the (001) surface of magnetite ideal for model studies of the catalytic activity of supported single atoms. In this study, we examine the adsorption and reaction of methanol on Fe_3O_4(001) and Pd/Fe_3O_4(001) surfaces using a combination of scanning tunneling microscopy, temperature programmed desorption, and x-ray photoelectron spectroscopy. We find that a monolayer of methanol saturates on Fe_3O_4(001) at a coverage of 5.8×10^{14} molecules/cm^2, which corresponds to one methanol per every surface Fe^{3+} ion. The majority of methanol desorbs molecularly by 280 K. Above 300 K, methanol dissociates to form methoxy and hydroxyl species.[2] The maximum coverage of methoxy that can be achieved is 1.2×10^{14} molecules/cm^2. The methoxy species form an ordered layer adsorbed on the Fe^{3+} sites above the subsurface cation vacancies. At elevated temperatures, the methoxy species react via one of two processes: recombining with hydroxyl to desorb as additional molecular methanol at 350 K, or further dehydrogenation to produce formaldehyde above 500 K. Production of formaldehyde is limited to 2.3×10^{13} molecules/cm^2. On single Pd atoms on Fe_3O_4(001), the production of formaldehyde above 500 K is suppressed while a new formaldehyde channel is observed at 300 K. Increasing the Pd atom concentration increases the magnitude of the low-temperature channel. Interestingly, the total amount of formaldehyde produced in these two channels remains constant throughout the range of Pd concentrations studied, indicating that the methoxy species are formed on the Fe_3O_4 substrate and Pd atoms only facilitate the conversion of methoxy species to formaldehyde. However, the appearance of the lower temperature reaction channel for formaldehyde shows that the Pd atoms lower the reaction barrier to dehydrogenate methoxy to formaldehyde by almost a factor of two.

1. R. Bliem et al. *Phys. Rev B***92,** 075440 (2015)
2. O. Gamba et al. *Top. Catal.***60,** 420 (2017)

8:20am **HC+SS-WeM2 Hydrogen Activation and Spillover on Single Palladium Atoms Supported on Fe_3O_4(001) Surface***, **Nassar Doudin**,* Pacific Northwest National Laboratory*; J. Cheng Liu,* Tsinghua University, China*; M.D. Marcinkowski, M.-T. Nguyen,* Pacific Northwest National Laboratory*; J. Li,* Tsinghua University, China*; V.-A. Glezakou,* Pacific Northwest National Laboratory*; G.S. Parkinson,* Vienna University of Technology, Austria*; R. Rousseau, Z. Dohnálek,* Pacific Northwest National Laboratory

Single-atom catalysts have recently attracted great attention due to their ultimate metal efficiency and the promise of novel properties. However, at the atomic level, little is known about their stability, interactions with the support, and mechanisms by which they operate. Recently it has been shown that on Fe_3O_4(001) surface, single metal atoms can be stabilized to temperatures as high as 700 K [1]. This high stability makes Fe_3O_4(001) a promising support for model studies of single atom catalysts. Here, we present a room-temperature study of H_2 dissociation on single Pd atoms on Fe_3O_4(001) followed by H atom spillover via scanning tunneling microscopy (STM) and density functional theory (DFT). The exposure to H_2 at 300 K results in the appearance of bright double protrusions located on surface iron (Fe_S) sites. Such protrusions were observed previously [2] following the adsorption of atomic H and hydroxyl formation (O_SH) on bare Fe_3O_4(001). By analogy, we attribute the features observed here to O_SH species. The DFT calculations further reveal that H_2 dissociates heterolytically and spills over both hydrogen atoms onto Fe_3O_4(001). When the exposure to H_2 is increased, the density of O_SH's is also observed to increase. With approximately every fourth surface oxygen atom hydroxylated, many areas show a local order with O_SH's spaced according to the (√2×√2)R45° surface reconstruction. STM data further indicate that H atoms diffusion is accelerated in the presence of coadsorbed water. At highest coverages of O_SH's (approximately every second oxygen atom hydroxylated), the reconstruction is lifted, and the Pd atoms become destabilized . These studies clearly demonstrate that single Pd atoms can efficiently dissociate H_2 that spills over onto a reducible oxide support that can be extensively hydroxylated.

[1] R. Bliem et al. Science 346, 6214 (2014).

[2] G. S. Parkinson et al. Phys. Rev. B 82, 125413 (2010).

8:40am **HC+SS-WeM3 Model Studies on Ligand-assisted Heterogeneous Catalysis***, **Swetlana Schauermann**,* Christian-Albrechts-University Kiel, Germany **INVITED**

Identifying the surface processes governing the selectivity in hydrogenation of α,β-unsaturated carbonyl compounds on late transition metals is crucial for the rational design of new catalytic materials with the desired selectivity towards C=O vs. C=C bond hydrogenation. In the present talk it will be shown that the selectivity of these reactions can crucially depend on the presence of specific ligand-like surface co-adsorbates. Specifically, I will present a mechanistic study on selective hydrogenation of acrolein over model Pd surfaces – both single crystal Pd(111) surface and Pd nanoparticles supported on a model oxide support.[1] We show for the first time that selective hydrogenation of the C=O bond in acrolein to form the desired reaction product – an unsaturated alcohol propenol – 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 highly selective towards propenol formation. By applying pulsed multi-molecular beam experiments and *in operando* IRAS we identified the chemical nature of the spectator and the reactive surface intermediate as oxopropyl and propenoxy species, respectively. The evolution of the surface concentration of the propenoxy intermediate monitored spectroscopically was found to closely follow the propenol formation rate detected in the gas phase.

In the second part, the catalytic surfaces modified with chiral adsorbates will be discussed. In heterogeneous catalysis, such chiral modification of the non-chiral metal surfaces allows to turn the catalytic processes asymmetric and produce enantiopure compounds. We will discuss the atomistic details of the chiral modification as well as the interaction between the chiral modifiers and the prochiral adsorbates on well-defined Pt(111) surface.

References:

1. Dostert, K.-H.et al, *J. Amer. Chem. Soc.* **2015**, *137*, 13496-13502.

9:20am **HC+SS-WeM5 *In situ* Structural Studies and Gas Phase Visualization of Model Catalysts at Work*, Sara Blomberg*[1]**, *J. Zetterberg, J. Zhou, J. Gustafson, E. Lundgren,* Lund University, Sweden

Catalysis is widely used in the production process of chemicals, pharmaceuticals, fuels or ammonia synthesis. The catalyst accelerates the chemical reaction but without being consumed. The materials system of a catalyst is complex and as a result, the catalytic process in most cases is not fully understood, and fundamental studies of the catalyst at operating conditions are close to impossible.

In the last decades, a number of *in situ* experimental techniques have been developed operating at semi-realistic condition to extend the fundamental knowledge on catalytic reactions and to bridge the pressure gap. We have therefore used Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) for surface and gas-phase studies and Planar Laser-induced Fluorescence (PLIF) for gas phase visualization.

Using APXPS to investigate the CO oxidation over a Pd(100) single crystal[2], we observe a pressure dependent CO desorption temperature, and therefore a pressure dependent ignition temperature of the reaction. The experiments were carried out by slowly increasing the temperature of the Pd(100) in a 1:1 ratio of CO and O_2 and systematically increasing the total pressure. The increasing ignition temperature of the catalyst is observed in conjunction with an increasing oxygen coverage on the surface measured immediately after the ignition. Remarkably, no CO could be detected neither in the gas phase nor adsorbed on the surface after the ignition of the reaction, despite a highly active surface.

To investigate the gas phase in more detail, we have developed PLIF, where an image of the gas distribution close to the surface is obtained [2]. PLIF was used to study *in situ* the change of the gas phase during CO oxidation, where the images visualize the build-up of a boundary layer of CO_2 close to the active surface, and the reaction is mass transfer limited by the diffusion of CO. Within this boundary layer the gas composition is significantly different as compare to the composition detected at the outlet of the reactor by a mass spectrometer (MS)[3]. The drastic drop in the CO pressure close to the surface explain the lack of detected CO in the APXPS experiments, which result in a partial pressure of CO below the detection limit of the APXPS.

[1] S. Blomberg et al. In Situ X-Ray Photoelectron Spectroscopy of Model Catalysts: At the Edge of the Gap, Phys Rev Lett, **110** (2013) 117601.

[2] Sara Blomberg *et alJ. Phys.: Condens. Matter***28** (2016) 453002

[3] J. Zetterberg et al. Spatially and temporally resolved gas distributions around heterogeneous catalysts using infrared planar laser-induced fluorescence. , Nat Commun, **6** (2015) 7076.

9:40am **HC+SS-WeM6 Adsorption, Thermal Stability, and Kinetics of Atomic Oxygen at Ag(111) and Ag(110) Surfaces*, Sara Isbill*[2]**, *S. Roy,* University of Tennessee Knoxville

Transition-metal surfaces are commonly used to catalyze transformations of small organic compounds, but the catalyst structures and catalytic mechanisms are not yet completely understood. Silver surfaces are important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards revealing the complex chemical pathways of oxidation reactions on silver surfaces, the role of subsurface oxygen (oxygen adsorbed just beneath the surface) in surface reconstruction and oxidative catalysis by silver has yet to be elucidated. In the present study, density functional theory (DFT) was used to probe the interactions of atomic oxygen with the surface and subsurface of Ag(111) and Ag(110) surfaces. The goal was to investigate adsorption, thermal stability, and kinetics of surface and subsurface oxygen at different coverages on the metal surfaces and examine their effects on the structural and catalytic properties of silver. On Ag(111), it was found that both surface and subsurface adsorption energies decreased with oxygen coverage, but surface adsorption weakened more drastically than subsurface adsorption. In contrast, on Ag(110), surface adsorption remained more favorable than subsurface adsorption at all studied coverages. Our thermodynamic and kinetic models of O/Ag(111) based on DFT-computed equilibrium constants and activation energies show that the stability of subsurface oxygen is sensitive to coverage, thereby indicating that the participation of subsurface oxygen in catalysis would strongly depend on coverage. Overall, our results provide valuable qualitative insight into the formation and motion of subsurface oxygen on Ag(111) and Ag(110) surfaces, the importance of metal-adsorbate charge transfer in these systems, and the possible roles of subsurface oxygen in catalytic oxidation by silver.

11:00am **HC+SS-WeM10 Understanding the Intrinsic Surface Reactivity of Multilayer vs. Single-layer PdO(101) on Pd(100)*, Jason Weaver*,** *V. Mehar,* University of Florida*; M. Kim,* Ohio State University*; M. Shipilin,* Lund University, Sweden*; M. van den Bossche,* Chalmers University of Technology, Gothenburg, Sweden*; J. Gustafson,* Lund University, Sweden*; L. Merte,* Chalmers University of Technology, Gothenburg, Sweden*; U. Hejral,* Lund University, Sweden*; H. Gronbeck,* Chalmers University of Technology, Gothenburg, Sweden*; E. Lundgren,* Lund University, Sweden*; A. Asthagiri,* Ohio State University

Understanding the intrinsic reactivity of different types of O-rich phases that form on Pd surfaces is central to developing accurate models of oxidation catalysis. In this talk, I will discuss results of a recent study in which we used temperature programmed reaction spectroscopy (TPRS) and surface IR spectroscopy (RAIRS) as well as DFT calculations to investigate the intrinsic CO oxidation activity of single and multiple-layer PdO(101) structures grown on Pd(100) in UHV. We find that CO binds more strongly on multiple vs. single-layer PdO(101) (~110 vs. 40 kJ/mol), and that CO oxidizes negligibly on single-layer PdO(101) whereas nearly 90% of a saturated layer of CO oxidizes on multiple layer PdO(101) during TPRS experiments. RAIRS further shows that CO molecules adsorb on both bridge and atop-Pd_{cus} sites (coordinatively-unsaturated Pd sites) of single-layer PdO(101)/Pd(100), while CO binds exclusively on atop-Pd_{cus} sites of multilayer PdO(101). Our DFT calculations reproduce the much stronger binding of CO on multiple layer PdO(101) as well as the observed binding site preferences, and reveal that the stronger binding is entirely responsible for the higher CO oxidation activity of multiple vs. single layer PdO(101)/Pd(100). We show that the underlying O-atom bonding partners, present only in multiple layer PdO(101), modify the electronic states of the Pd_{cus} atoms in a way that enhances the CO-Pd_{cus} bonding. Lastly, we show that a simple kinetic model, with energetics determined from the present study, predicts that the intrinsic CO oxidation rates achieved on both single and multilayer PdO(101)/Pd(100) can be expected to exceed the gaseous CO diffusion rate to the surface during steady-state CO oxidation at elevated pressures, even though the intrinsic reaction rates are 4-5 orders of magnitude higher on multiple vs. single layer PdO(101)/Pd(100). Our findings help to resolve seemingly disparate conclusions about the CO oxidation activity of the single and multiple layer PdO(101) structures, as determined from previous *in situ* vs. UHV measurements, and highlight the importance of characterizing the intrinsic reactivity of catalyst surfaces for developing first-principles kinetic models that can accurately reproduce surface reactivity over a wide range of conditions.

11:20am **HC+SS-WeM11 Simultaneous Study of Catalyst Structure, Gas Phase and Morphology*, Sebastian Pfaff*,** *J. Zhou, S. Albertin,* Lund University, Sweden*; M. Shipilin,* Stockholm University, Sweden*; J. Gustafson, S. Blomberg, E. Lundgren, J. Zetterberg,* Lund University, Sweden

CO oxidation has long been studied as a model reaction for catalysis diagnosis. In recent time, increased focus has been given to study well-defined single crystal surfaces to further investigate the details of the involved reaction mechanisms[1]. During the past years, new techniques have been developed to study both the surface structure and gas phase in a semi-realistic environment such as High Energy Surface X-Ray Diffraction (HESXRD)[2] and Planer Laser Induced Fluorescence (PLIF)[3]. HESXRD is a technique well suited to gain knowledge about the surface structure, but without any macroscopic spatial resolution. Planar Laser Induced Fluorescence (PLIF) is a technique which excels at determining the structure and composition of the gas phase. One of the main advantages of this technique is its high spatial and immediate temporal resolution. Additionally, LED surface reflectance techniques have been developed, which provide a simple way of producing a macroscopic map of the entire single crystal, clearly visualizing changes on the surface[4].

In this work, the mentioned techniques were combined at the beamline P07 at PETRA III while performing CO oxidation over a Pd(100) single crystal sample. We have shown a clear spatial correlation between a reduced surface reflectance and an increased CO2 concentration in the gas phase. Additionally, through the sub-second temporal resolution of PLIF, we have

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[1] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

[2] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

determined the delay between a measurable change of the surface structure using HESXRD and a change in gas composition as the catalyst switches between high and low activity.

References

1. Freund, H.-J., et al., *CO Oxidation as a Prototypical Reaction for Heterogeneous Processes.* Angewandte Chemie International Edition, 2011. **50**(43): p. 10064-10094.

2. Gustafson, J., et al., *High-Energy Surface X-ray Diffraction for Fast Surface Structure Determination.* Science, 2014. **343**(6172): p. 758-761.

3. Zetterberg, J., et al., *Spatially and temporally resolved gas distributions around heterogeneous catalysts using infrared planar laser-induced fluorescence.* Nature Communications, 2015. **6**: p. 7076.

4. Zhou, J., et al., *Simultaneous Imaging of Gas Phase over and Surface Reflectance of a Pd(100) Single Crystal during CO Oxidation.* The Journal of Physical Chemistry C, 2017. **121**(42): p. 23511-23519.

11:40am **HC+SS-WeM12 New Catalysis for Light Alkanes – From Methane Functionalization to Light Akenes*, Johannes Lercher,*** Pacific Northwest National Laboratory and TU München, United States of America/Germany **INVITED**

The abundant availability of light alkanes opened new opportunities to synthesize light alkenes and oxygenates, challenged only by the high dispersion of the carbon sources, requiring dedicated processes. Three different principal catalysis pathways will be discussed, the conversion of methane to methanol, the oxidative dehydrogenation of ethane and the dehydrogenation of propane to propene, eventually followed by aromatization. For the three approaches it will be shown, how the atomistic understanding of the catalyst properties including an atomistic description of the active site by combining electron microscopy and X-ray absorption spectroscopy and the molecular pathways by identifying elementary steps via NMR spectroscopy and isotope labeling allows to drastically develop catalysts and catalytic pathways. Combining rigorous kinetics with spectroscopy allowed for all three cases to describe rates linked to specific active sites and maximize their concentration. The potential and limitations of this fundamental approaches to discover new catalysts and improve existing will be discussed.

Industrial Physics Forum
Room 101B - Session IPF+AS+BI+NS-WeM
IoT Session: Bioanalytics, Biosensors and Diagnostics

Moderators: Anna Belu, Medtronic, Sally McArthur, Swinburne University of Technology and CSIRO

8:40am **IPF+AS+BI+NS-WeM3 Harnessing Bacteria for Fabrication of Photoelectrodes and Pressure Sensors***, Y. Feng, K.E. Marusak, Y. Cao, E. Ngaboyamahina, J. Glass, L. You,* ***Stefan Zauscher,*** Duke University **INVITED**

Conventional methods for material fabrication often require harsh reaction conditions, have low energy efficiency, and can cause a negative impact on the environment and human health. In contrast, structured materials with well-defined physical and chemical properties emerge spontaneously in diverse biological systems. However, these natural processes are not readily programmable. By taking a synthetic-biology approach, we demonstrate a method for the fabrication of semiconducting, transition metal nanoparticles (NPs) with tunable bandgap and useful photoelectric properties, through bacterial precipitation. Surface analytic measurements revealed that our bacterially precipitated CdS NPs are agglomerates of quantum dots (QDs) in a carbon-rich matrix. We discovered that the precipitation conditions of the bacteria can be tuned to produce NPs with bandgaps that range from quantum-confined to bulk CdS. We determined the photoelectrochemical properties and energy band structure of thin films prepared from these NPs by electrochemical measurements. By taking advantage of the organic matrix, which is residual from the biosynthesis process, we fabricated a prototype photo-charged capacitor electrode by incorporating the bacterially precipitated CdS with a reduced graphene oxide sheet. Furthermore, we show the programmable, three-dimensional (3D) material fabrication using pattern-forming bacteria growing on top of permeable membranes as the structural scaffold. When the bacteria are equipped with an engineered protein that enables the assembly of gold (Au) nanoparticles into a hybrid organic-inorganic dome structure, the resulting hybrid structure functions as a pressure sensor that responds to touch. We furthermore show that the response dynamics are determined by the geometry of the structure, which is programmable by the membrane properties and the extent of circuit activation. By taking advantage of this property, we demonstrate signal sensing and processing using one or multiple bacterially assembled structures. Our work provides the first demonstration of using engineered cells to generate functional hybrid materials with programmable electronic properties and architectures for energy conversion, energy storage, and for signal sensing and transduction.

9:20am **IPF+AS+BI+NS-WeM5 Surface Chemistry and Surface Analysis: Their Importance and Application in Industrial Genomics*, Fiona Black*,** Illumina Inc. **INVITED**

Understanding the genome has the power to revolutionize health. However, building robust and scalable tools to interrogate single base variants with high robustness requires a system level approach to integrate surface patterning and activation, biosensing, and imaging. This talk will review how micro-patterning, bioanalytical controls, surface analytical techniques and measurement tools are applied in an industrial setting to develop and manufacture cutting edge systems for sequencing and genotyping applications

11:00am **IPF+AS+BI+NS-WeM10 Design and Evaluation of Organosilica Nanosensors for Continuous Molecular Monitoring in Complex Biological Environments*, Simon Corrie*,** Monash Univ., Melbourne AU **INVITED**

Continuous monitoring of biomarkers in biological environments is a key challenge for the development of biosensors capable of providing real-time feedback. Sensors capable of continuous pH monitoring have already found applications in detection of bacterial infections and have potential for aiding in treatment of dynamic diseases. Nanoparticle based “optodes” have emerged as sensitive and tuneable biosensors, using chromo/ionophores to generate analyte-specific changes in fluorescence spectra in a dynamic and reversible manner. Current key limitations of these materials include leaching of reagents from the nanoparticles over time, combined with poor colloidal stability in biological fluids.

Organosilica is a promising material for developing stable biosensors, allowing simple control over size, interfacial chemistry and porosity. This presentation will describe the development of a core-shell nanoparticle containing a mixture of covalently incorporated pH-sensitive (shell) and pH-insensitive (core) fluorescent dyes. Attachment of anti-fouling polymers is used reduce aggregation and biofouling in biological media. Fluorescence analysis of the nanoparticles reveals that the shell/core fluorescence ratio is highly sensitive to pH over a physiological range with the response time <1s. The sensitivity and dynamic range can be tuned by varying material properties of the shell (primarily thickness and porosity). We will present our latest results on the application of these nanosensors for continuous, real-time monitoring, including in bacterial cultures, subcutaneous mouse “tattoos," and in 3D hydrogel scaffolds.

11:40am **IPF+AS+BI+NS-WeM12 Optoregulated Biointerfaces*, Aránzazu del Campo*,** INM-Leibniz Institute for New Materials, Germany **INVITED**

Cells interact with their microenvironment by engaging membrane receptors with complementary partners at the surrounding matrix or at other neighbouring cells. These receptor complexes, often associated to cytoskeletal structures, allow exchange of biochemical and mechanical information. The ability to quantify this exchange is crucial for our understanding of cellular behavioru and responses to external factors. Using model biointerfaces with optoregulated interaction possibilities, selective membrane receptors in living cells can be addressed in situ, i.e. on a sensor surface, while quantifying specific cellular responses. Light-regulated tools to apply and sense cell biochemical and mechanical interactions will be presented.

MEMS and NEMS Group
Room 202B - Session MN+NS+PS-WeM
IoT Session: Multiscale Manufacturing: Enabling Materials and Processes

Moderators: Susan Burkett, The University of Alabama, Sébastien Hentz, CEA/LETI-University Grenoble Alpes, France

8:00am **MN+NS+PS-WeM1 Miniaturizing 3D Printed Microfluidics: State-of-the-Art and Outlook*, Greg Nordin,*** Brigham Young University **INVITED**

While there is great interest in 3D printing for microfluidic device fabrication, the challenge has been to achieve feature sizes that are in the truly microfluidic regime (<100 µm). The fundamental problem is that commercial tools and materials, which excel in many other application areas, have not been developed to address the unique needs of microfluidic device fabrication. Consequently, we have created our own stereolithographic 3D printer and materials that are specifically tailored to meet these needs. We show that flow channels as small as 18 µm x 20 µm can be reliably fabricated, as well as compact active elements such as valves and pumps. With these capabilities, we demonstrate highly integrated 3D printed microfluidic devices that measure only a few millimeters on a side, and that integrate separate chip-to-world interfaces through high density interconnects (up to 88 interconnects per square mm) that are directly 3D printed as part of a device chip. These advances open the door to 3D printing as a replacement for expensive cleanroom fabrication processes, with the additional advantage of fast (30 minute), parallel fabrication of many devices in a single print run due to their small size.

8:40am **MN+NS+PS-WeM3 A Novel Inkjet Printing Technology Based on Plasma Conversion of Metal-Salt Based Inks for the Fabrication of Microfabricated Sensors***, Y. Sui, R.M. Sankaran,* ***Christian Zorman****,* Case Western Reserve University

Inkjet printing is a leading additive manufacturing method to produce patterned metal thin films on flexible substrates. The most commonly-used inks consist of colloidal nanoparticle suspensions that employ organic molecules to stabilize the nanoparticles from agglomeration and precipitation. High temperature (>200°C) treatment is used after printing to remove the insulating organics and sinter the nanoparticles. The thermal step can limit printing on polymers such as PDMS, paper, and other temperature-sensitive substrates. Moreover the selection of metals is limited by those available in nanoparticle suspensions, with the most popular being Ag.

In this paper, we present the development of an ink-jet printing process that uses a particle-free, stabilizer-free ink and low-temperature plasma to produce electrically conductive metallic patterns on temperature-sensitive substrates. The inks are comprised of a metal salt, a solvent, and a viscosity modifier tailored to enable printing using a Dimatix DMP3000 series printer. The as-printed structures are treated with a low-pressure argon plasma which serves to convert the metal salt-based structures to metal structures with conductivities that approach bulk values. To date, we have demonstrated the process for Sn, Pb, Bi, Cu, Pt, Ag, Pd, and Au-based inks. The plasma-treated structures exhibit a high degree of porosity that can be as high as 70%, making them particularly well suited for use as active elements in microfabricated sensors. The extended paper will present details pertaining to the printing process, material characterization and testing of mechanical, chemical and biological sensors fabricated by this printing process.

9:00am **MN+NS+PS-WeM4 Full Wafer Thickness Through Silicon Vias for MEMS Devices***,* ***Andrew Hollowell****, E. Baca, D. Dagel, M.B. Jordan, L. Menk, K. Musick, T. Pluym, J. McClain,* Sandia National Laboratories

A significant amount of development has been achieved integrating TSVs with standard silicon (Si) substrates; however, there are unique challenges associated with integrating TSVs with MEMS substrates. Industry has achieved TSV integration through a dependence on substrate thinning, a TSV reveal approach. However, often these MEMS devices depend on the thickness of the substrate for controlling the radius of curvature of the substrate, such as throughout Sandia's ultra-planar multilevel MEMS technology (SUMMiT^{TM}). TSV filling relies on tight control of the fluid kinetics during the electroplating process and the ability to balance the diffusion of Cu^{2+} and organic suppressor molecules throughout the depth of the via in order to realize a void-free fill of the TSV. In this work we have extended the filling model for 60 µm deep TSVs, developed by Tom Moffat and Dan Josell, up to 675 µm deep TSVs.

In addition to the thickness constraints for MEMS integration, often MEMS devices are realized through unique release processes and are dependent on high temperature anneals. The most common release process is a hydrofluoric acid (HF) based release to selectively remove supporting oxide films and preserve the Si features that make up the MEMS components. The necessity to release structure in selective etchants presents additional challenges for integrating TSVs with MEMS components. We have overcome this challenge through the integration of additional capping layers which are selectively removed after the MEMS release. In order to accommodate the need for high temperature anneals we have removed the use of metal in the MEMS device and instead used doped silicon. The Cu TSVs are then integrated with the device after all the high temperature anneals are complete, making direct electrical contact to the doped Si. In this work, we present our integration approach for mating Cu TSVs with doped Si MEMS contacts and our plating approach for superfilling 675 µm deep, 100 µm wide TSVs.

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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9:20am **MN+NS+PS-WeM5 Scaling from Die Level to Full 150 mm Wafer TSV Filling through Fluid Dynamics Modeling and Current Controlled Deposition***,* ***Ehren Baca****, M.B. Jordan, L. Menk, K. Musick, P. Yeh, A.E. Hollowell,* Sandia National Laboratories

In this work we have developed a novel methanesulfonic acid (MSA) based electrolyte with a single suppressor additive for filling 100 µm diameter 675 µm deep through silicon vias (TSVs). Contrary to conventional three-additive systems we have achieved bottom up super filling of these large TSVs with a single suppressor additive. This bottom up super filling mechanism is dependent on a strict balance between applied potential and diffusion of both suppressor molecules and Cu^{2+} ions. The bottom up deposition was developed through die level plating experiments on sample sizes approximately 1 in^2. We control the solution replenishment by connecting the sample, both electrically and mechanically, to an aluminum rod and rotating the sample in solution. The rotation rate is directly correlated to the velocity of solution moving across the opening of the vias and therefore related to the solution replenishment inside the TSVs. At first a potentiostatic approach was used to supply a sufficient potential to break down the suppressor with a reference electrode in our plating cell. Mapping the current, during deposition allowed us to develop a galvanostatic plating process.

Experiments were performed to scale this plating process to be compatible with production level electroplating tools. The fluid dynamics and applied current are significantly different on production plating tools. The tools do not come equipped with reference electrodes and in some cases, they have multiple anodes for current partitioning to control the uniformity of the electric field. Further, the wafer rotates about the center of the wafer and baffles are integrated into the tool to control the uniformity of a fountain type fluid replenishment system. With the wafer rotated about its center, there is a large variance in the velocity of fluid at different radii along the wafer. In this work, we present a set of scaling experiments performed on die with incremental increases in sample size to clearly map the die level plating parameters to a full wafer plating tool and achieve uniform TSV filling across a 150 mm wafer.

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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9:40am **MN+NS+PS-WeM6 Batch Level Electroless Under Bump Metallization for Singulated Semiconductor Die***,* ***Matthew Jordan****, E. Baca, J. Pillars, C. Michael, A.E. Hollowell,* Sandia National Laboratories

Multi project-wafers (MPWs) allow multiple customers to share the cost of a manufacturing run from an advanced semiconductor foundry. This offers a cost-effective solution for low volume the fabrication or prototyping of application specific integrated circuits (ASICs). This practice is especially appealing for those in academia or government that often only require small quantities of devices for research or niche applications. With many products on a wafer, all the products must adhere to the same strict design rules. In practice this means that the final metallization is made using AlCu. This presents challenges for advanced packaging of MPW die as AlCu is not compatible with conventional flip chip solder because of oxidation of the AlCu metal. Further complicating the integration of MPW die is the fact that they are singulated prior to delivery, preventing the use of lithography, and thus ruling out the deposition and patterning of solder-compatible metals over the AlCu. This leaves the use of electroless plating schemes to prepare MPW die for 2.5D/3D die stacking.

We propose a batch process to facilitate MPW die processing through the electroless under bump metallization (UBM) process. This process includes passivation of the Si die sidewalls post dicing, MPW die mounting, batch Zn or Sn immersion followed by electroless Ni, electroless Pa, immersion Au (ENEPIG) or electroless Ni, immersion Au (ENIG) UBM deposition for reliable, UBM deposition. We have demonstrated 2.5D integration of batch processed, AlCu finished die that have UBM deposited using this process to an interposer using electroplated Cu pillars bumps and Au bumps.

Supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

11:00am **MN+NS+PS-WeM10 MEMS-based Atomic Force Microscopy Probes: From Electromechanical to Optomechanical Vibrating Sensors***, **Bernard Legrand,*** LAAS-CNRS, France*; L. Schwab,* LAAS-CNRS, Univ Tououse, France*; P. Allain, I. Favero,* MPQ, CNRS, Univ Paris Diderot, France*; M. Faucher, D. Théron,* IEMN, CNRS, Univ Lille, France*; B. Walter,* Vmicro SAS, France*; J.P. Salvetat,* CRPP, CNRS, Univ Bordeaux, France*; S. Hentz, G. Jourdan,* CEA-LETI, France **INVITED**

Scanning probe microscopy has been one of the most important instrumental discoveries during the last quarter of the last century. In particular, atomic force microscopy (AFM) is a cross-disciplinary technique able to provide sample morphology down to the atomic scale. It offers invaluable tools to support the development of nano-sciences, information technologies, micro-nanotechnologies and nano-biology. For more than 20 years, boosting the scan rate of AFM has been an increasingly important challenge of the community. However still today, performing routine and user-friendly AFM experiments at video rate remains unreachable in most cases. The conventional AFM probe based on a micro-sized vibrating cantilever is the major obstacle in terms of bandwidth and resonance frequency.

Following a brief description of the context of the work, the talk will first describe the development of AFM probes based on MEMS devices that make use of ring-shaped microresonators vibrating above 10 MHz. A focus will be dedicated to the electrical detection scheme. Based on capacitive transduction and microwave reflectometry, it achieves a displacement resolution of 10^{-15}m/√Hz, allowing the measurement of the thermomechanical vibration of the MEMS AFM probes in air. Imaging capability obtained on DNA origamis samples at a frame rate greater than 1 image/s will be shown as well as investigation of block copolymer surfaces to elucidate the tip-surface interaction when vibration amplitudes are lower than 100 pm.

In the following, our recent research direction at the convergence of the fields of micro/nanosystems and VLSI optomechanics on silicon chips will be presented. Optomechanical resonators allow indeed overcoming the resolution limitation imposed by usual electromechanical transduction schemes. Here, we will introduce fully optically driven and sensed optomechanical AFM probes which resonance frequency is above 100 MHz and Brownian motion below 10^{-16}m/√Hz, paving the way for high-Speed AFM operation with exquisite resolutions at sub-angstrom vibration amplitudes.

11:40am **MN+NS+PS-WeM12 Suppressing Secondary Grain Growth in $Sc_{0.125}Al_{0.875}N$ Using a CMOS Compatible Electrode***, **Giovanni Esteves,** M. Berg, M.D. Henry, B.A. Griffin, E.A. Douglas,* Sandia National Laboratories

The electromechanical response of AlN can be enhanced by doping Sc into AlN up to ~43%. Challenges arise in processing high Sc doped AlN films due to the presence of secondary grain growth. Templating $Sc_xAl_{1-x}N$ (ScAlN) from a platinum bottom electrode has shown immense success in yielding highly textured *c*-axis ScAlN without the presence of secondary grain growth. However, platinum is not complementary metal-oxide-semiconductor (CMOS) compatible which makes it unattractive to those in industry. There is a need for a new bottom electrode that suppresses secondary grain growth while maintaining CMOS compatibility. In this work, $Sc_{0.125}Al_{0.875}N$ and AlN films were grown on various underlying CMOS compatible metal stacks. Optimal film microstructure and texture was obtained for films deposited on highly textured {111} $AlCu_{0.05}$ bottom metal. AlN and ScAlN thicknesses were 750 nm and 850 nm and showed rocking curves of 0.81° and 1.09°, respectively. Atomic force microscopy was used to determine the presence of secondary grain growth and film roughness. The success of this bottom metal stack is attributed to lattice matching and low surface roughness which allows for highly oriented *c*-axis textured AlN and ScAlN. This work presents a metal stack that allows for the creation of higher Sc-doped AlN films while maintaining a high-quality microstructure and texture. Therefore, allowing for commercialization of Sc-doped AlN technologies which are capable of higher electromechanical coupling coefficients than AlN devices.

This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Nanometer-scale Science and Technology Division
Room 203A - Session NS+2D+AN+MN+MP+SE-WeM

Micro, Nano and Opto Mechanics

Moderators: Robert Ilic, National Institute of Standards and Technology, Alokik Kanwal, NIST Center for Nanoscale Science and Technology

8:20am **NS+2D+AN+MN+MP+SE-WeM2 The Collective Behavior of Large Ensembles of Coupled MEMS Cantilevers with Varying Natural Frequencies***, **Christopher Wallin,*** National Institute of Standards and Technology, Center for Nanoscale Science and Technology*; N. Dick,* Tel Aviv University, Israel*; R. De Alba, D.A. Westly,* National Institute of Standards and Technology, Center for Nanoscale Science and Technology*; S. Grutzik,* Sandia National Laboratories*; A.T. Zehnder, R.H. Rand,* Cornell University*; V.A. Aksyuk,* National Institute of Standards and Technology, Center for Nanoscale Science and Technology*; S. Krylov,* Tel Aviv University, Israel*; B.R. Ilic,* National Institute of Standards and Technology, Center for Nanoscale Science and Technology

The collective behavior of nonlinear, coupled micro- and nano-electromechanical (M/NEMS) resonators has been shown to exhibit a host of nontrivial dynamics including abrupt pattern switching, multistability, hysteresis, intrinsically localized modes, and synchronization. Additionally, M/NEMS resonator arrays are extremely responsive to environmental perturbations making them excellent candidates for sensing applications when operated linearly. With our work, we investigate the collective dynamics of coplanar interdigitated arrays of prismatic microcantilevers operating in both the nonlinear and linear regimes.

Two opposing, partially interdigitated cantilever arrays with 100 cantilevers apiece were fabricated using a silicon–on–insulator wafer. The device consists of a unique geometry in which each array has cantilever lengths expanding linearly across the device in opposite directions giving a distribution of natural frequencies. The arrays were engineered to allow for large scale, nonlinear out-of-plane beam deflections through the removal of the entire silicon handle layer beneath the active array area.

For sufficiently large drive amplitudes, the resonators begin oscillating via combination parametric resonance (CPR) across the entire array. The CPR driven oscillations occur across a broad frequency band. The tunable coupling between nearest-neighbor cantilevers through fringing electrostatic fields provides a mechanism to vary the CPR response. Due to the sizable deflections, the device's nonlinearities are apparent including hysteresis effects. Our experimental results are supported and expanded by the development of a reduced order model based on the Galerkin decomposition which generates the leading features of our data including the CPR band.

When operating in the linear regime, the natural modes of the array have localized characteristics whereby a limited number of beams oscillate at each of the natural mode frequencies. Operating the device at higher harmonics increases mode separation as the propagation bands stretch. The distinct resonant peak separation coupled with the spatially confined modal response make higher harmonic operation of tailored, variable length cantilever arrays well suited for a variety of resonant based sensing applications.

8:40am **NS+2D+AN+MN+MP+SE-WeM3 Piezoelectric Optomechanical Systems***, **Krishna Coimbatore Balram**,* University of Bristol, UK **INVITED**

Nanoscale optomechanical systems, which rely on the strong interactions between co-localised optical and mechanical modes in nanoscale cavities, have been explored for a wide variety of applications ranging from sensing to signal transduction [Aspelmeyer et al., Rev. Mod. Phys. (2014)]. In this talk, I will discuss piezoelectric optomechanical platforms for efficient signal transduction between the radio frequency (RF) and optical domain. We use GaAs as our model platform (Balram et al., Optica (2014), Nature Photonics (2016), Phys. Rev. Applied (2017)) and discuss some of the research opportunities and challenges in this field, especially as we move towards higher mechanical frequencies (> 10 GHz).

9:20am **NS+2D+AN+MN+MP+SE-WeM5 Absolute Deflection Measurements in a MEMS/NEMS Fabry-Perot Interferometry System***, **Roberto De Alba**, C.B. Wallin, G. Holland,* National Institute of Standards and Technology*; S. Krylov,* Tel Aviv University, Israel*; B.R. Ilic,* National Institute of Standards and Technology

Micro- and nano-electromechanical systems (MEMS/NEMS) are among the most sensitive devices for detection of ultra-weak forces, masses, and displacements. The small scale of these structures affords them very high frequencies (MHz to GHz), high quality factors, rich nonlinear phenomena, and many other beneficial traits that make them ideal as sensors and testbeds of fundamental physics. Fabry-Perot laser interferometry is a widespread and robust technique for probing MEMS/NEMS devices because it is non-invasive and provides exceptional motion sensitivity (≈ 1 pm/Hz$^{1/2}$) from DC to roughly 100 MHz. This technique utilizes the silicon substrate beneath the MEMS/NEMS device as a static reference mirror; doing so provides common-mode noise rejection in contrast to interferometers that use an external reference mirror. Furthermore, this technique is compatible with a wide range of MEMS/NEMS materials, from common insulators and conductors to graphene and other atomically-thin membranes.

Despite the many strengths of this experimental technique, it suffers from two main drawbacks. Firstly, the measured signal becomes highly nonlinear for device displacements larger than $\lambda/4$, where λ is the laser wavelength. Secondly, because the silicon backplane is immovable, there is no simple or established technique for calibrating device motion. As such, published results utilizing this setup typically report deflection in “arbitrary units.” In this work, we focus on fully characterizing the nonlinear aspects of a MEMS/NEMS Fabry-Perot interferometer and developing a generalized approach to calibrate device motion based the wavelength of light. We will demonstrate how to quickly and accurately determine both static and dynamic MEMS/NEMS deflection by measuring reflected laser power in the time domain. We will further show how a single calibration (made in the large-amplitude regime) can be applied to subsequent measurements taken at lower amplitudes as well as to measurements taken in the frequency domain (e.g. by a lock-in amplifier). Lastly, we will demonstrate the capability of imaging the first three vibrational modes of a MEMS cantilever by using a scanning laser.

9:40am **NS+2D+AN+MN+MP+SE-WeM6 Silicon on Insulator Electrostatically Actuated Bistable Cantilevers for Resonant Displacement/Acceleration Sensing***, O. HaLevy, E. Benjamin, N. Krakover, Y. Kessler, **Slava Krylov**,* Tel Aviv University, Israel

Resonant accelerometers incorporating vibrating beams demonstrate higher sensitivity and better robustness when compared to their statically operated counterparts. Electrostatic softening of the beams electrostatically coupled to the proof mass allows to enhance sensitivity of the resonant accelerometers. The displacement of the proof mass affects the gap between the mass and the beam and results in the beam’s frequency change, which is maximal in the vicinity of the critical limit points of the voltage-deflection curve. The use of the snap-through buckling for this purpose is attractive since it is fully reversible and does not involve contact. While double-clamped curved bistable beams designed to demonstrate snap-through behavior can serve as resonant acceleration sensors [1], they suffer from high sensitivity to temperature and residual stress.

In this work we report on a design and fabrication of an electrostatically actuated bistable resonant cantilever [2], which demonstrates low sensitivity to the temperature and to the residual stress. The concept is based on the tailoring of the actuating force in such a way that the beam in its initial “as fabricated” configuration is positioned in the vicinity of the critical point. This is achieved by designing the actuating electrodes to be significantly thicker that the beam. Our reduced order (RO) Galerkin and coupled finite elements (FE) models results show that the frequency to deflection sensitivity of the L = 150 μm long, h = 16 μm wide and d = 1 μm thick cantilever can reach 20 Hz/nm. This is equivalent to the frequency to acceleration sensitivity of 388 Hz/g, obtained for the case of a 4 mm × 4 mm × 20 μm proof mass.

While the model results are promising, fabrication of the device incorporating the beams and the electrodes of the different thicknesses is challenging. We demonstrate fabrication of the 50 μm thick electrodes and ≈6 μm thick cantilevers from the same device layer of a Silicon on Insulator (SOI) wafer. Two-stage deep reactive ion etching (DRIE) process was used for an initial patterning of the electrodes and of the cantilever and for the thinning of the beams. We discuss the details of the fabrication process and preliminary experimental results.

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[2] N. Krakover, S. Krylov, “Bistable Cantilevers Actuated by Fringing Electrostatic Fields,” *ASME Journal of Vibration and Acoustics*, **139**(4), 040908-040908-10, 2017.

11:00am **NS+2D+AN+MN+MP+SE-WeM10 Electron-Photon-Phonon Hybrid Systems Based on Compound Semiconductor Mechanical Resonators***, **Hiroshi Yamaguchi**,* NTT Basic Research Laboratories, Nippon Telegraph and Telephone Corporation, Japan **INVITED**

The use of compound semiconductor heterostructures as the elastic materials in the fabrication of micro/nanomechanical resonators has advantages, such like the improvement of mechanical properties through strain engineering, optomechanical transduction through carrier-mediated coupling, and piezoelectrically controllable nonlinearity [1]. The hybrid properties play the essential role in the operation where the different excitations of phonons, photons, and electrons are mutually interacted. In this invited talk, I will review our recent activities studying the electronic [2], photonic [3], and phononic [4] functions in GaAs-based mechanical resonators.

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11:40am **NS+2D+AN+MN+MP+SE-WeM12 Size Dependent Mechanics of Elastomers***, **Le Li**, N. Alsharif, K.A. Brown,* Boston University

Elastomers are fascinating materials owing to the fact that their mechanical properties are dictated by entropy. Due to their low modulus, chemical compatibility, and ease of processing, they are widely applied in fields from soft lithography to medical devices. While it is well accepted that they exhibit fascinating size-dependent mechanical properties when confined to thin films, the structure-property relationships that govern confined elastomers are difficult to unambiguously determine due to the mechanical influence of rigid support structures and unavoidable contributions from adhesion. As a result, a consensus regarding the moduli of elastomeric thin films has not emerged. Here, we present a combined computational and experimental approach to measure the true mechanical properties of thin elastomer films. First, we utilize extensive finite element simulations to determine a correction to the Hertzian contact model that depends upon a dimensionless film thickness and the polymer Poisson’s ratio. In order to verify this correction, films composed of three different thermoplastics were studied using an atomic force microscopy (AFM) nanoindenting. Interestingly, all three were observed to soften when confined to films thinner than 100 nm, in agreement with literature reports of buckling experiments. To explore softer elastomeric materials that exhibit categorically different behavior, we extended this correction to the Johnson-Kendall-Roberts (JKR) model that considers adhesion in contact mechanics. Elastomer thin films with different crosslink densities were studied using AFM nanoindentation and finite element simulation to determine their moduli. We observed a drastic stiffening on all elastomeric films when they were confined to sub-micrometer thicknesses. More importantly, modulus of all sub-100 nm elastomer films converges to the same trend regardless of bulk crosslink density. We present a hypothesized molecular model explaining this behavior. These results shed new light on the nanomechanics of elastomers and provide a general process for exploring size-dependent mechanics in polymers.

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic
Room 202A - Session PC+AS+BI+EM+PB+SS-WeM

Novel Approaches and Challenges of Interfaces

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), Xiao-Ying Yu, Pacific Northwest National Laboratory

8:00am **PC+AS+BI+EM+PB+SS-WeM1 Probing Chemical Species and Potential Profiles of Electrified Interfaces*, Ethan J. Crumlin,*** Advanced Light Source, Lawrence Berkeley National Laboratory **INVITED**

Interfaces play an important role in nearly all aspects of life, and are essential for electrochemistry. Electrochemical systems ranging from high temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. This talk will focus on our use of ambient pressure XPS (APXPS) to directly probe the solid/liquid electrochemical interface. In particular, I will discuss how we were able to probe the potential drop within the electrochemical double layer (EDL) as well as the potential of zero charge under polarization conditions. This unique approach was accomplished by measuring spectral changes observed in both the electrolyte (water) and a neutral spectator probing molecule (pyrazine). By combining these experiments with numerical simulations provided the ability to discern the shape of the electrochemical double layer profile as a function of both electrolyte concentration and applied potentials. Extending beyond the EDL, I will highlight some of our recent investigations into both the oxygen evolution reaction on a platinum electrode as well as a magnesium electrode in a non-aqueous electrolyte. Information gained from these studies will aid in the guided design and control of future electrochemical interfaces.

8:40am **PC+AS+BI+EM+PB+SS-WeM3 Observation of Electron Transfer in Riboflavin Reduction by In Situ Liquid SIMS*, Rachel Komorek*,** *X.F. Yu, Z.H. Zhu, X-Y. Yu,* Pacific Northwest National Laboratory

Riboflavin is of vital significance in living processes as a precursor of the two important coenzymes flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD).[1] The isoalloxazine ring in riboflavin plays an important role in energy supplementation and cellular respiration, since it has the capability to accept electrons in some redox reactions.[2] Understanding riboflavin reduction could potentially bring insight into the electron transfer process between cell surfaces and conductive materials. Thus, the electrochemical reduction process of riboflavin has drawn increasing attention. In this study, the riboflavin reduction mechanism in an aqueous solution has been investigated using time-of-flight secondary ion mass spectrometry (ToF-SIMS) with the electrochemical cell.[3, 4] Positive and negative ion mode mass spectra were used to depict the molecular information of species dissolved in the electrolyte. The distribution of key reduction intermediates were mapped at the electrode-electrolyte interface using dynamic depth profiling. To examine product formation as a function of applied potentials, measurements were made by holding the potential at 0, -0.3, 0.3, and 0.6 V respectively, once interesting electrochemistry was determined using the cyclic voltammogram. Furthermore, gold and graphite electrodes were both used in our experiment to investigate if the electrode surface plays a role in in the electrochemical reaction mechanism. Preliminary spectral principal component analysis (PCA) results have shown key chemical distinctions in the electrolyte at 0, -0.3, 0.3, and 0.6 V. Selected peak spectral PCA is required to gain a better understanding of this observation, which will allow for a more comprehensive chemical profile of the electron transfer process in riboflavin redox reactions.

Key words: in situ liquid SIMS, SALVI, riboflavin reduction, electrochemistry, electron transfer

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9:00am **PC+AS+BI+EM+PB+SS-WeM4 Electrowetting of Liquid Drops Revisited by XPS*, Sefik Suzer,*** *P. Gokturk, B. Ulgut,* Bilkent University, Turkey

Electrowetting behavior of liquid drops has been followed in-situ and in-vacuum using XPS in a chemically resolved fashion, under both dc and ac excitations. Various Liquid drops, compatible with the UHV conditions, consisted of an Ionic Liquid (DEME-TFSI), Poly-ethylene-glycol (M.W. ~600 amu) and their mixtures. For the dielectric substrate, a ~300 nm thick silicon oxide (SiO_2/Si) without and with a thin hydrophobic coating (CYTOP) has been employed. XPS data have been recorded both in the conventional scan- and also in the fast (<1s) snap-shot modes. Intensity and position of the peaks, representing the liquid drops (F1s in the case of the IL, or C1s/O1s of the PEG) as well as those of the substrates (Si2p for the oxide only and F1s for the hydrophobic coated one) have been recorded under various electrical excitations. Under ac excitation at a fixed frequency, intensity modulations in the XPS peaks reveal geometrical changes of the drops, while the peak position modulations reveal electrical potentials developed. Monitoring position modulations as a function of the changes in the ac frequency ($10^{-2} – 10^{5}$ Hz) allows us to tap into ionic, dipolar and electrical contributions of the dielectric susceptibility of both the liquid drops and the substrates. Experimental details and various application will be presented and discussed.

*This work is partially supported by TUBITAK through Grant No. 215Z534

9:20am **PC+AS+BI+EM+PB+SS-WeM5 Probing Interfaces in Heterogeneous Catalysts at Atomic Scale: Current and Emerging STEM Techniques**, *M. Chi,* ***Wenpei Gao*,** Oak Ridge National Laboratory **INVITED**

Chemical reactions take place on the surfaces and interfaces of heterogeneous catalyst systems. Depending on the phase of the reactant, the reactive interfaces include those between solid-gas, solid-liquid, and triple-phase interfaces of solid-gas-liquid. At these interfaces, the catalyst provides active sites where the reactants are adsorbed, activated, and converted to new chemical species that are eventually released from the catalyst surface. The ability of catalysts in promoting these reactions is determined by the surface binding energy, which can be modified by tuning the interfacial atomic arrangements or by forming new interfaces, e.g., forming core-shell structures. Understanding the formation of these interfaces during synthesis and their structural and chemical evolution during operation are important to the rational design of future high-performance catalysts. Probing these dynamically evolving interfaces at a sufficient spatial resolution, however, presents many challenging. Recent work on elucidating the formation and the operation mechanisms of interfaces in precious metal-based heterogeneous catalysts using *in situ* atomic-scale scanning transmission electron microscopy (STEM) techniques will be discussed. Several emerging STEM-based methods, such as vibration spectroscopy and atomic-scale differential phase contrast imaging that are currently under development within the microscopy community will be introduced, and their prospective influence on future studies to design functional interfaces in heterogeneous catalysts will be discussed.

Acknowledgements: Research supported by the Center for Nanophase Materials Sciences, which is a U.S. Department of Energy (DOE) Office of Science User Facility.

11:00am **PC+AS+BI+EM+PB+SS-WeM10 From 2D to Advanced 3D Surface Functionalization using Self-limiting Reactions in the Fluidized Bed Reactor Technology*, Didier Arl*,** *T. Da Cunha, N. Adjeroud, K. Menguelti, M. Gerard, D. Lenoble,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

The integration of novel functional nanomaterials like high specific surface powders in polymeric or inorganic matrices requires a fine control of their properties. The design of these nanoscopic agents is linked to the development of nanotechnology processes which can be transferred from planar substrates to complex 3D surfaces. In this framework we showed how self-limiting reactions inspired by Atomic Layer Deposition can be applied to functionalize powder by using a specifically designed Fluidized Bed Reactor. A specific interest has been given to work in non-saturated regime with nickel or Cobalt acetylacetonate to obtain well controlled metal nanocatalysts of 5-10nm diameter. Depending on the process window, some interesting properties have been demonstrated such as ferromagnetic behavior or the systematic recover of the Metal-Carbide phase that increase the throughput of Carbon Nanotubes growth. These activated nanostructures can expressly improve the electrical, the thermal or the mechanical properties of some related composites depending on how some processing parameters such as exposure time, pressure or local temperature can be tailored.

Plasma Science and Technology Division
Room 104B - Session PS+AS+EL+EM+SE-WeM
Current and Future Stars of the AVS Symposium I

Moderator: Eric A. Joseph, IBM Research Division, T.J. Watson Research Center

8:20am **PS+AS+EL+EM+SE-WeM2 Invited Talk-Future Stars of AVS Session: Ellipsometry at THz Frequencies: New Approaches for Metrology and Metamaterial-based Sensing*, Tino Hofmann*[1]*,*** University of North Carolina at Charlotte

Spectroscopic ellipsometry at terahertz frequencies has seen substantial advancements over the last several years. Now, instruments are available which allow precise measurements of the material's complex dielectric function including its anisotropy. This access to accurate electromagnetic material properties at THz frequencies is essential for the development of increasingly advanced THz optical systems and a prerequisite for the design and manufacturing of optical elements for this spectral range.

In this talk I will give an overview of recent developments in the implementation of THz ellipsometry and focus on applications where THz ellipsometry contributed valuable material parameters. In combination with external magnetic fields generalized THz ellipsometry allows the accurate measurement of the optical Hall effect. The optical Hall effect enables the precise determination of the free charge carrier properties effective mass, mobility, and density in semiconductor heterostructures at THz frequencies without the need of electrical contacts and will be discussed in detail.

The exploration of novel physical phenomena observed in artificially structured metamaterials and the application thereof is of interest due to its relevance for the design and fabrication of novel THz optical elements and sensors. Metamaterials have attracted continued interest for almost two decades due to their unique electromagnetic properties, which can differ substantially from their constituents and often do not even exist in naturally occurring materials. We have demonstrated that although being orders of magnitude smaller than the probing wavelength, metamaterials composed of highly-ordered 3-dimensional metal nanostructures exhibit a strong anisotropic optical response at THz frequencies. I will discuss how these interesting optical properties may be used for novel THz sensor and device designs.

8:40am **PS+AS+EL+EM+SE-WeM3 Invited Talk-Future Stars of AVS Session: Remote Epitaxy – The Future for Stackable SiC Electronics*, Rachael Myers-Ward*[2]*,*** U.S. Naval Research Laboratory*; J. Kim,* Massachusetts Institute of Technology*; M.T. DeJarld,* US Naval Research Laboratory*; K. Qiao, Y. Kim,* Massachusetts Institute of Technology*; S.P. Pavunny, D.K. Gaskill,* U.S. Naval Research Laboratory

Ideally, electronic heterostructures from dissimilar materials leads to enhanced functionality. Yet, experimentally forming these heterostructures is challenging due to lattice or thermal coefficient of expansion mismatch leading to defect formation or thermally driven atomic diffusion resulting in cross-doping and gradual junction transitions. These challenges may be overcome with the discovery of remote epitaxy and 2D layer transfer [1]. Here, SiC epitaxy is performed on epitaxial graphene as the electrostatic fields from the substrate penetrate the graphene and guide adatom registry. The film is easily peeled away since the graphene is not bonded to either the substrate or epilayer; the epilayer is then van der Waals bonded to a different material enabling new functionality. We will present experimental results on the remote epitaxy of SiC, illustrating potential quantum science applications.

There are three necessary steps to create remote epitaxy. The first is to grow epitaxial graphene on SiC, followed by transferring the graphene to a desired substrate (if different from SiC), and finally the growth of the remote epitaxial layer. If the remote epitaxy is to be SiC, which is the focus of this paper, the second step is not needed. Epitaxial graphene (EG) was first synthesized on 4H- and 6H-SiC in a horizontal hot-wall CVD reactor between 1540 and 1580 °C in 10 slm of Ar and 100 mbar [2]. The growth temperature was dependent upon the offcut of the substrate, where substrates with higher offcuts require a lower growth temperature to ensure 1 ML of EG, which is desired to assist in SiC adatom registry during growth. SiC remote epitaxy was then performed on the EG using silane (2% in H_2) and propane precursors, where the SiC polytype replicated the underlying substrate. In an effort to transfer the remote SiC epi/EG to another substrate such as SiO_2/Si, a metallization step was performed. Thin Ti and/or Ni layers were initially deposited followed by a thicker high stress metal to create strain and aide in removing the remote SiC epi/EG from the SiC substrate [1]. Once transferred, the metal was removed via a metal etch.

In this work, we will discuss the important parameters needed for successful remote SiC epitaxy, such as metallization, graphene thickness and remote epitaxy growth temperature. The epitaxial morphology characterized by SEM and Nomarski microscopy and graphene coverage and transfer evaluated by Raman spectroscopy will be presented.

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9:00am **PS+AS+EL+EM+SE-WeM4 Invited Talk-Future Stars of AVS Session: Low-Temperature Growth for 3D Integration of van der Waals Materials*, Christopher L. Hinkle*[3]*,*** University of Texas at Dallas

The integration of novel logic and memory devices, fabricated from van der Waals materials, into CMOS process flows with a goal of improving system-level Energy-Delay-Product (EDP) for data abundant applications will be discussed. Focusing on materials growth and integration techniques that utilize non-equilibrium, kinetically restricted strategies, coupled with in-situ characterization, enables the realization of atomic configurations and materials that are challenging to make but once attained, display enhanced and unique properties. These strategies become necessary for most future technologies where thermal budgets are constrained and conformal growth over selective areas and 3-dimensional structures are required.

In this work, we demonstrate the high-quality MBE heterostructure growth of various layered materials by van der Waals epitaxy (VDWE). The coupling of different types of van der Waals materials including transition metal dichalcogenide thin films (e.g., WSe_2, WTe_2, $HfSe_2$), helical Te thin films, and topological insulators (e.g., $Bi_{-2}Se_3$) allows for the fabrication of novel electronic devices that take advantage of unique quantum confinement and spin-based characteristics. We demonstrate how the van der Waals interactions allow for heteroepitaxy of significantly lattice-mismatched materials without strain or misfit dislocations. We will discuss TMDs, Te, and TIs grown on atomic layer deposited (ALD) high-k oxides on a Si platform as well as flexible substrates and demonstrate field-effect transistors with back-end-of-line (<450 °C) and even flexible plastics (<200 °C) compatible fabrication temperatures. High performance transistors with field-effect mobilities as high as 700 $cm^2/V\text{-}s$ are demonstrated. The achievement of high-mobility transistor channels at low processing temperatures shows the potential for integrating van der Waals materials into new technologies.

This work was supported in part by the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA. This work is also supported in part by NEWLIMITS, a center in nCORE, a Semiconductor Research Corporation (SRC) program sponsored by NIST through award number 70NANB17H041.

9:20am **PS+AS+EL+EM+SE-WeM5 Invited Talk-Future Stars of AVS Session: Engineering the Properties at Heusler Interfaces*, Jason Kawasaki*[4]*,*** University of Wisconsin - Madison

The Heusler compounds are a ripe platform for engineering and discovering emergent electronic, magnetic, topological, and ferroic properties at crystalline interfaces, either with other functional Heuslers or with compound semiconductor or oxide substrates. In these applications, the ability to control interfaces with near atomic level control is of tantamount importance; however, challenges such as interdiffusion have hampered their development. Here, I will discuss our efforts to control the properties of Heusler interfaces using precision growth by molecular beam epitaxy (MBE). Results will be presented in three areas: (1) the use of epitaxial strain to stabilize the hexagonal phase of several polar metal candidates, (2) the use of monolayer graphene diffusion barriers to enable

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[1] **Future Stars of the AVS**

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high temperature growth and performance of spintronic devices, and (3) the phase segregation of ferromagnetic FeV nanostructures from a semiconducting FeVSb matrix with coherent epitaxial interfaces. Together, these examples illustrate the power of epitaxy and interfaces in controlling the properties of Heuslers and other intermetallic compounds, and integrating them onto commonly used semiconductor substrate platforms.

9:40am **PS+AS+EL+EM+SE-WeM6 Invited Talk-Future Star of AVS Session: Atom Probe Tomography for 3D Semiconductor Devices Applications***,* ***Ajay Kumar Kambham***[1]*,* GLOBALFOUNDRIES U.S. Inc.

Device structures are rapidly scaling down to the nanometer regime with the ongoing development in semiconductor device technology. Along with this, it is ever critical need to engineer dopant profiles and to define the formation of junctions in Metal-oxide field effect transistors (MOSFETs). This is increasingly challenging considering the severity of short channel effects (SCEs). Indeed, one type of SCE in MOSFET devices 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 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 role of APT and how elemental distributions vary depending on process conditions along with the challenges involved in sample preparation.

11:00am **PS+AS+EL+EM+SE-WeM10 Invited Talk-Future Stars of AVS Session: Three-Dimensional Imaging of Complex Oxide Interfaces***,* ***Divine P. Kumah***[2]*,* North Carolina State University

Complex oxide materials have a wide range of exciting tunable electronic and magnetic phases including ferroelectricity and superconductivity. The ability to fabricate atomic layers of complex oxides has led to the formation of novel interfaces and heterostructures of scientific and technological interest. The functional properties are usually correlated to sub-Angstrom structural perturbations at these interfaces. In this talk, a non-destructive synchrotron X-ray three-dimensional imaging technique will be applied to understand thickness-dependent electronic and magnetic transitions which occur in rare-earth manganite films with thicknesses on the order of an atomic layer. We show that structural distortions arising due to the electrostatic interfacial boundary conditions of the thin films are related to their thickness-dependent phase transitions. Based on these results, we show that heterostructures can be designed by molecular beam epitaxy to tune the atomic-scale structure of the manganite films to achieve robust ferromagnetism in atomically-thin layers. These results have important implications for the design of oxide-based spintronic devices and provide an important pathway for the realization of novel functional materials.

11:20am **PS+AS+EL+EM+SE-WeM11 Invited Talk-Future Stars of AVS Session: lluminating Physics of Magnetron Sputtering Discharges***,* ***Matjaz Panjan***[3]*,* Jozef Stefan Institute, Slovenia

Magnetron sputtering is an established plasma technology for the deposition of thin films. In general, the technique is classified by the voltage supplied to the cathode; this can be continuous (DCMS), pulsed (HiPIMS) or oscillatory (RFMS). The distinction is also made with respect to the geometry of the magnetron source (e.g., circular, linear, cylindrical) and the magnetic field configuration (balanced or unbalanced). Despite the differences in the cathode operation, geometry and, magnetic field configuration, the underlying principle that forms dense magnetron plasma is the same. The central feature of magnetron sources is a crossed magnetic and electric field arrangement, which captures electrons close to the cathode. In such configuration, electrons gyrate around the magnetic field lines, bounce from the electric field of the sheath and drift in the azimuthal direction. The entrapment of electrons increases the plasma density close to the cathode (e.g., forming a ring-shaped plasma above the circular magnetron) and enhances the sputtering rate. Experiments using high-speed imaging and other techniques revealed that magnetron plasma is not azimuthally homogenous instead, it forms dense plasma structures called spokes. These structures have been extensively studied over the past few years and have changed our understanding of several physical processes in the magnetron discharges. Spokes are observed for a wide range of discharge conditions, magnetron geometries and are an essential feature of all operational regimes [1-3]. They commonly form periodic patterns, have an arrowhead-like shape with an arrow pointing in the **E**×**B** direction, and travel with azimuthal velocities of several km/s. In the talk, I will present efforts to understand the physics of spokes and magnetron discharges in general. In particular, I will discuss spatial distribution of the plasma potential [4] and the influence it has on the transport of charged particles [5], sputtering process and overall sustainability of the discharge. I will demonstrate that electric fields associated with spokes cause localized re-energization of electrons and thus help to sustain magnetron discharge. Spokes also influence energy and spatial distribution of ions and therefore indirectly affect the thin film growth.

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11:40am **PS+AS+EL+EM+SE-WeM12 Peter Mark Memorial Award: Plasma-bio Interactions: Investigating Mechanisms to Enable New Applications***,* ***Peter Bruggeman***[4]*,* University of Minnesota **INVITED**

Cold non-equilibrium atmospheric pressure plasmas (CAPs) have received a lot of attention in the last decades due to their huge potential for biomedical applications including wound healing, cancer treatment, dental treatments and disinfection and decontamination of heat sensitive materials [1]. These applications are due to the near ambient gas temperature at which CAPs can be produced and their high reactivity, involving the production of numerous reactive oxygen and nitrogen species [2]. Many applications require controlled interactions of plasma with bacteria, virus and mammalian cells or tissue that enable selectivity between healthy and cancer cells or in the treatment of bacteria on healthy tissue or food samples for which off target effects needs to be minimized. A controlled selectivity might be the greatest challenge for these applications and requires a detailed understanding of the underlying plasma-bio-interaction mechanisms. In this framework, my group in collaboration with microbiologists has performed detailed studies of the interactions of CAP with virus, bacteria and mammalian cells. Our research shows that controlling the gas phase plasma chemistry can lead to significant different biological responses of the living organisms [3-6]. The outcomes of these studies allow unraveling chemical pathways responsible for plasma-bio interactions and linking plasma kinetics to plasma-bio interactions. These insights are of invaluable importance for the development of applications in the field of plasma medicine.

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Acknowledgements

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[1] **Future Stars of the AVS**

[2] **Future Stars of the AVS**

[3] **Future Stars of the AVS**

[4] **Peter Mark Memorial Award Winner**

Plasma Science and Technology Division
Room 104A - Session PS+EM-WeM

Advanced Patterning

Moderators: Jeffrey Shearer, IBM Research Division, Albany, NY, Yiting Zhang, KLA-Tencor

8:00am **PS+EM-WeM1 Study of High Selective Silicon Nitride Etching Mechanisms in Remote Plasmas: Impact of Wafer Temperature***, **Emilie Prevost**,* STMicroelectronics, France*; L. Vallier, G. Cunge,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; C. De Buttet,* CEA-LETI, France*; S. Lagrasta,* STMicroelectronics, France*; C. Petit-Etienne,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

Nowadays in the Semiconductor industry, challenging applications often requires ultra-high selectivity etching processes. Wet processes are often used but have drawbacks and show limitations in high aspect ratio features. One alternative possibility is to use chemical downstream etching plasmas. In this work, NF_3/O_2 downstream plasmas are used to etch selectively Si_3N_4 towards SiO_2 in high aspect ratio patterns (over 100).

In NF_3/O_2 plasmas, we observe that the wafer temperature (T°) has a considerable (but non linear) impact on the etching selectivity. When T° is raised from 40°C to 100°C, the selectivity first drop and then increase again, with a marked minima at 70°C. Indeed, the etching rate of Si_3N_4 and SiO_2 have a different behavior with T°: while the SiO2 etch rate increase slowly and continuously with T°, the Si_3N_4 etch rate first drop between 40 and 70 °C and then increases again at higher T°. This effect is attributed to two mechanisms in competition, the etching led by atomic fluorine and surface passivation via oxidation. To better understand the nonlinear behavior of the Si_3N_4 etch rate, the etching mechanisms of Si_3N_4 as a function of T° was investigated by plasma (VUV absorption spectroscopy) and surface diagnostics (Ellipsometry,XPS and AFM).

Angular XPS analysis show that the Si_3N_4 surface oxidation is minimal at low T° (40°C). As the wafer T° is increased, the thickness of the oxidized layer also increases rapidly until it reaches its maximum (about 5 nm) at 70°C. This is attributed to an enhanced diffusion of the O atoms produce by the plasma in the Si_3N_4 material. At higher T° the thickness stays constant but the amount of O in the layer decreases. In the NF_3/O plasma, atomic fluorine are responsible for the etching of both Si3N4 and SiO2 but with a natural selectivity. Therefore, the surface oxidation of the Si_3N_4 surface during etching is going to slow down the nitride etch rate and the thicker this layer is the smaller the etch rate will be (F atoms must diffuse through this layer to reach Si_3N_4). Therefore, when the T° is increased the Si_3N_4 etch rate initially drops because the SiO_x layer at its surface becomes thicker. Above 70°C the layer thickness stays constant but its degree of oxidation is decreasing when T° is increased: this explain why the Si_3N_4 etch rate increases again above 70°C. Hence the nonlinear behavior of the selectivity is due to a competition between the etching (by atomic fluorine) and surface oxidation, which strongly depends on T°. We highlighted via our research an important change on the etching mechanism at 70 °C, explained by the rapid formation of a thick oxidized layer.

8:20am **PS+EM-WeM2 Mechanism of Highly Selective SiO_2 Etching over Si_3N_4 using a Cyclic Process with BCl_3 and Fluorocarbon Gas Chemistries***, **Miyako Matsui**,* Hitachi Ltd., Japan*; K. Kuwahara,* Hitachi High-Technologies Corp., Japan

Multiple patterning techniques require extremely high selectivity to various materials and controllability of cross-sectional pattern profiles with atomic scale precision. In these fine patterning techniques, SiO_2 etching over Si_3N_4 requires an advanced process to form a thinner protection layer on Si_3N_4. For example, SiO_2 atomic layer etching with the fluorocarbon (FC) passivation of C_4F_8 plasma followed by Ar^+ bombardment has been investigated [1]. To achieve a high selectivity to Si_3N_4 using conventional FC plasma, the thickness and composition of the FC film should be controlled to protect only the Si_3N_4 surface from reaction with the FC film [2]. In our previous study, we proposed a cyclic SiO_2 etching process over Si_3N_4 by using BCl_3 and FC gas chemistries [3]. BCl_3 plasma was applied because it was expected to form a thin protection layer, which was suitable for selective etching at fine patterns when a low wafer bias was used. The thin protection layer formed by BCl_3 plasma was also expected to inhibit the spontaneous etching of Si_3N_4 by F radicals.

In this study, we investigated a cyclic process using BCl_3 and fluorocarbon gas chemistries for a fine pattern structure with a space width of 20 nm. The relationships between etching parameters and cross-sectional pattern profiles were also analyzed to control the pattern profiles. This process alternately performs two steps: an adsorption step using BCl_3 mixed-gas plasma and an etching step using $BCl_3/CF_4/Ar$ plasma with applying a wafer bias. The mechanism of the cyclic process was investigated by analyzing the surface chemistry at each step. At the adsorption step, a thicker BCl_x layer was formed on the Si_3N_4 surface than on the SiO_2 surface. Then, CCl_x films were formed on both surfaces at the etching step. We found that the thicker BCl_x layer formed on Si_3N_4 at the adsorption step protected Si_3N_4 from etching by reaction of BCl_x with CF_x and F radicals at the etching step. The B atoms in the BCl_x layers desorbed from the surfaces by forming BF_x, BCl_xF, and CCl_x. In contrast, the BCl_x layer became thinner on SiO_2 than that on Si_3N_4 to promote ion-assisted etching of SiO_2. This is because the BCl_x component has high reactivity with SiO_2, and the CF_x component was also consumed by the etching reaction with SiO_2. We also found that ion-flux should be controlled to etch without shoulder-loss, and ion-energy should be controlled to etch without footing shape at the bottoms of the pattern.

[1] D. Metzler et al., J. Vac. Sci. Technol. A **32**, 020603 (2014).

[2] M. Matsui et al., J. Vac. Sci. Technol. A **19**, 2089 (2001).

[3] M. Matsui et al., Jpn. J. Appl. Phys. **57**,(2018) to be published.

8:40am **PS+EM-WeM3 DSA Patterning for and Beyond CMOS***, **Patricia Pimenta Barros**,* CEA-LETI, France*; N. Posseme,* CEA, LETI, France*; S. Barnola,* CEA-LETI, France*; R. Tiron,* CEA-LETI, MINATEC, France*; A. Gharbi, MA. Argoud, Z. Chalupa, M.-G. Gusmao-Cacho,* CEA-LETI, France*; A. Paquet,* Arkema, France*; F. Delachat,* CEA-LETI, France*; C. Nicolet, C. Navarro,* Arkema, France **INVITED**

The continuous increase of CMOS device density has led to new 3D architectures. For the sub-7nm nodes, Leti investigates the interest of Tri-gate, Ω-gate and stacked nanowires architectures for better electrostatic control at aggressive dimensions [1, 2]. These new architectures bring a set of etching challenges at the integration level (from active, spacer, Si/SiGe removal) and require innovative etching solutions, such as gas or bias pulsing and atomic layer etching (ALE). In this paper, an overview of the main challenges and solutions for Si/SiGe stacked NW patterning will be exposed.

The active patterning of dense stacked nanowires have been already demonstrated by Leti using the Sidewall Image Transfer (SIT) technique [3]. In this paper, we will focus on the Directed Self Assembly (DSA) of block-copolymers (BCPs) that is considered as a cost-effective and complementary solution to conventional or EUV lithography [4, 5]. Herein, stacked Si nanowires are patterned using a DSA UV-assisted graphoepitaxy approach. Chemoepitaxy and graphoepitaxy approaches, which are the two ways to perform DSA, will be benchmarked. The transfer of ultra-small patterns using high-chi BCPs materials (pitch <20nm) will be also reported.

Based on LETI's FDSOI background, we are investigating new architectures such as steep slope devices, mechanical switches or single electron devices in a CMOS compatible flow. They are all studied in a CMOS co-integration perspective to enable the hybrid logic field [6]. In this paper, we will show that DSA patterning could be a good candidate for some applications beyond CMOS such as Single Electron Transistor devices or nano-membranes manufacturing.

[1] Coquand, R., et al., Symposium on VLSI Technology, pp. T226-T227 (2013)

[2] Barraud, S., et al., Symposium on VLSI Technology, Kyoto, pp. T230-T231 (2013)

[3] Gaben, L., et al., International Conference on Solid State Devices and Materials, 1108 - N-2-2, pp1108-1109 (2015)

[4] Jeong, S-J., et al., Materials today 16 (12), 468-476 (2013).

[5] Guerrero, D. J., Solid State technology (2017)

[6] Barnola, S, et al., Proc. SPIE 9054 (2014)

9:20am **PS+EM-WeM5 Composition Modulation of SiGe for Si/SiGe Dual Channel Fin Application***, **Yohei Ishii**,* Hitachi High Technologies America Inc.*; Y.-J. Lee,* National Nano Divice Laboratories*; W.-F. Wu,* National Nano Device Laboratories*; K. Maeda,* Hitachi High Technologies America Inc.*; H. Ishimura,* Hitachi High-Technologies Taiwan Corp.*; M. Muira,* Hitachi High-Technologies Corp.

As a consequence of downscaling to follow Moore's law, device structure was changed from conventional planar structure to Fin-type Field Effect Transistors (FinFETs) to achieve higher drive current and lower leakage current. In sub-10nm processes, it is necessary to further improve FinFETs electrical performance. A promising approach is to replace silicon fins with a new material, such as silicon germanium, which enhances carrier mobility [1]. In Si/SiGe dual channel FinFETs, Si is used in n-FETs, while SiGe is used in p-FETs. Therefore, it is necessary to understand the difference in etching characteristics between Si and SiGe. Recently, we have developed an etching process to selectively etch Si over SiGe, and proposed the etching mechanism [2]. This etching technique proved to adjust not only the Si and SiGe pattern CDs (Si CD> SiGe CD and vice versa), but also Si and SiGe etched depth (Si etched depth < SiGe etched depth and vice versa), using Si/SiGe dual channel fin pattern samples.

As for the electrical performance of SiGe, it is important to form Si-rich SiGe surface at the SiO2/SiGe interface, because interface states play important role on sub-threshold characteristics [3]. There are several methods to form Si rich surface, such as thin Si cap epitaxial growth over SiGe fin [4] or H2 anneal-induced Si segregation [5]. However, it remains difficult to achieve the surface without the formation of a thick Si layer, which acts as a parasitic channel. In addition to that, avoiding Ge diffusion into Si cap layer is also an issue.

In this presentation, we propose a low-temperature process for achieving atomically controlled Si rich surface by utilizing plasma treatment to induce SiGe composition modulation at SiGe surface. We will also present a method to flexibly control the composition of SiGe surface (from Ge-rich surface to Si-rich surface) by utilizing plasma treatments. Details of the study will be discussed in this presentation.

[1] D. Guo, et. al., VLSI Tech. Dig., p.14, 2016

[2]. Y. Ishii et. al., Jpn. J. Appl. Phys. (Accepted)

[3]. C. H. Lee et. al., IEDM Tech. Dig., p.31.1.1., 2016

[4]. H. Mertens, et al., VLSI Tech. Dig., p.58, 2014

[5] L. Rudkevich, et. al., Phys. Rev. Lett. Vol.81 p. 3467 (1998)

9:40am **PS+EM-WeM6 Etching Mechanisms of Si Containing Materials in Remote Plasma Source using NF3 based Gas Mixture**

*, **Erwine Pargon**, V. Renaud, C. Petit-Etienne, L. Vallier, G. Tomachot, G. Cunge, O. Joubert,* Univ. Grenoble Alpes, CNRS, LTM, Grenoble, France*; J.-P. Barnes, N. Rochat,* Univ. Grenoble Alpes, CEA, LETI, Grenoble , France

The introduction of new 3D designs (fin FETs, nanowire..) for sub-10 technological nodes bring new challenges for etch applications. Contrary to planar devices, 3D devices require more isotropic etch capabilities with high selectivity between different materials . Remote plasma source (RPS) which is based only on chemical mechanisms offers great capability for etch applications requiring high etch selectivity such as removal of SiN spacer in 3D device or fabrication of Si or SiGe horizontal nanowire for gate all around device. NF3 based gas mixtures are frequently used to etch Si containing materials in a RPS process. In this paper, we propose to investigate the etching and selectivity mechanisms of Si containing materials (SiN, SiO_2, SiGe and Si) in RPS process using NF3/NH3 or NF3/H2 gas mixture. In this study, the hydrogen content of SiN and SiO_2 materials is modulated by using different deposition techniques (LPCVD, PECVD..). The etching experiments are performed in an industrial RPS reactor. The substrate temperature can be varied between 40 and 200°C. The etching kinetics are in real time thanks to in situ kinetic ellipsometry. The results show that the etching of both SiN and SiO_2 materials in NH_3/NF_3 remote plasma proceeds through the formation of $(NH_4)_2SiF_6$ salts on the material surface that consume the pristine material. Similarly to oxidation processes, the consumed thickness of material is proportional to the thickness of the salt layer. The real time monitoring of the SiN and SiO_2 etching reveals that the etching proceeds in three phases. First, the reactive species absorb on the material surface but without consuming it. The delay before the materials starts to be etched increases with substrate temperature and decreases if the surface is rich in O and/or H, conveying that these elements act as a catalysis of the salt formation. During the second phase, the material is etched rapidly through the salt layer. During this phase, the material consumption depends on the substrate temperature and nature, as well as the plasma conditions. Finally during the third phase, the materials are consumed less rapidly because the reactive species have to go through the salt layer before reaching the salt/material interface. The etching kinetics in the third phase are almost independent on the substrate temperature, material, and plasma conditions. The key to get infinite etch selectivity of SiN over SiO_2 and SiO_2 over SiN is to tailor the substrate temperature and the surface functionalization. High etch selectivity of SiGe over Si can be easily achieved in NH3/NF3 remote plasma. Adding H2 in the mixture allows to reverse the trend.

11:00am **PS+EM-WeM10 Precise Control of Silicon Nitride Spacer Etching Selectively to Silicon for 3D CMOS Device**

*, V. Ah-Leung, N. Possémé, **Olivier Pollet**, S. Barnola,* CEA-LETI, France

With transistors size scaling down, device processing requirements become more and more stringent. For technology node beyond 14 nm, one of the most critical step is the spacer etching. It requires a perfect anisotropy (no CD loss) without damaging [1] nor consumption of the exposed material like silicon, silicon germanium and oxide [2,3]. In planar transistor, the silicon or silicon germanium consumption is limited by the short over-etch process (30-50%). However for vertically stacked wires3D devices, the silicon fin is directly exposed during the removal of the silicon nitride on the active area sidewalls. This is the major issue since in this case, important over etch is required (>200%) to fully remove the residues at the bottom of the fin. Therefore, the spacer etch is considered today as one of the most challenging etch process for 2D but more especially 3D devices.

Today, current fluorocarbon etch chemistry (like CH3F/CH4/O2) are no longer suitable for 3D CMOS integration where long overetch is necessary.

In this context, we propose to introduce a new cyclic etch process of silicon nitride selectively to silicon to fulfill the stringent etch requirements described above [4].

This cyclic process is composed of two steps. A first step consists in silicon nitride etching till to top of the silicon fin. XPS analyses performed on blanket films (Silicon nitride and Si) reveal that a thin reactive layer is formed at the SiN surface, while an important deposition is observed at Si surface. This deposition at the Si surface is dependent of the process time. A second step (CHF3 based chemistry) allows partially removing the deposition on top of Si while etching the silicon nitride. Thanks to this new approach silicon nitride is linearly etched as a function of the number of cycles while the silicon film consumption is below 1.5nm. The selectivity reached by this new process is >100.

The impact of the different process step times and number of cycles on SiN and Si surface composition has been analyzed by XPS and will be presented. A proof of concept on vertically stacked wires patterned wafer will show that the silicon nitride spacer can be fully removed on the sidewall of the fin with limited impact on the silicon consumption/damage.

[1] N. Kuboi, T. Tatsumi, T. Kinoshita, T. Shigetoshi, M. Fukasawa, J. Komachi, and H. Ansai, J. Vac. Sci. Technol. A **33** (6), 061308 (2015).

[2] B. E. E. Kastenmeier, P. J. Matsuo, and G. S. Oehrlein, J. Vac. Sci. Technol. A **17** (6), 3179 (1999).

[3] K. Eriguchi, Y. Nakakubo, A. Matsuda, Y. Katao, K. Ono, IEEE Electr. Device L. **30** (7), 712 (2009).

[4] N.Posseme, S.Barnola, patent pending

11:20am **PS+EM-WeM11 A Study on the Distortion of Poly Si Nano Hole Profile with High Aspect Ratio in sub X nm**

*, **Jin Won Lee**, J.Y. Lee, K.J. Seong, T.S. Kwon, H.H. Jeong, S.S. Hong, D.W. Han, B.R. Lim, A.R. Ji, Y.M. Oh, J.C. Park,* Samsung Electronics, Republic of Korea

As the Critical Dimension (CD) of Semiconductor becomes smaller, process using new materials is being developed and multi-patterning processes are required to overcome the limitations of lithography. However, only a few of them have been adapted to mass-production of the semiconductor because they costs highly and are complex. As a result, Researches on Si materials (SiN, SiO_2, Poly-Si) widely used in semiconductors have been actively conducted.

In this study, we will describe the etch process with excellent LER (~ 1) by removing the distortion which causes various problems and securing the vertical profile in the Poly-Si nano hole with the high aspect ratio (1:50) in sub X nm. HBr based Etch is favorable for Poly Si Etch because it has a high selectivity between Poly-Si and SiO_2. However it has tendency to cause clogging $Si_XBr_YO_Z$ byproducts which aggravate the open margin and profile control. By the way, the etch profile is also deteriorated due to irregularly crystallized grains, which is a character of Poly-Si and they might induce etch stop it is severe. Unlike HBr based etch, Cl2 based etch tends to be less polymerizing and less reactive thus it causes less clogging which is less effective by the poly grain and is effective to improve the profile. We adopted Cl2 based multi cycle etch over HBr based etch to secure the characteristics of the vertical profile with etch stop free.

Distortion must be solved in order to improve the LER, which is an important factor that affects not only the vertical profile but also the electrical characteristics of semiconductor of device. In general, the etch rates increases with increased process temperature and the distortion tends to be improved. However, in our study, the hole distortion is improved and more vertical profile is led at low temperature. This can be explained by the difference in the re-deposition tendency of byproduct. When the temperature is high, a large amount of byproduct, that occurs after etch, is more re-deposited on the upper part than the lower part because the convective phenomenon becomes more active and the sticking coefficient of the hole side wall decreases. As a result, the clogging becomes worse, and the hole side wall cannot be re-deposited uniformly. CD tends to be smaller. Profile tends to be positive and LER tend to be worse. On the contrary, if the process temperature is low, the sticking coefficient of the hole side wall increases, and the re-deposition is performed well. Since it is totally re-deposited in the hole side wall, it is confirmed the CD is increased and a vertical profile is foamed and the LER is improved.

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11:40am **PS+EM-WeM12 Etching Recipe Optimization Using Machine Learning***, **Takeshi Ohmori**, H. Nakada, M. Ishikawa, N. Kofuji, T. Usui, M. Kurihara,* Hitachi, Ltd., Japan **INVITED**

The development of semiconductor fabrication processes has been prolonged due to constantly evolving nano-scale 3D devices. This lengthy development period has driven up the cost of semiconductor devices, and the process development needs to be sped up in order to reduce the cost.

Along with time modulation of plasma generation and bias power and an increase in the number of gas species, continuous improvement of the control functions of a plasma etcher has been made to provide accurate nano-scale etching. A set of parameters for the control functions is called a recipe, which is used as input data for the etcher. Etching accuracy can be improved by increasing the number of parameters in the recipe. However, it is difficult to optimize the recipe for obtaining a target etch profile when there are many parameters.

In this work, we present two types of exploration method for recipe optimization using machine learning: one using etching profile data [1] and the other using feature data related to the etching profile [2]. These were developed to assist the development of the etching process and to reduce the time period of the development, respectively.

In the method using the profile data, a recipe is optimized through the repetition of an optimization cycle that consists of learning the relationship between the profiles and the recipes, predicting the recipes to obtain a target profile, performing etching experiments with the predicted recipes, and adding the experimental results to the learning data. In this cycle, kernel ridge regression is used as the learning engine and a Si trench pattern is used to examine the exploration method. By using the predicted recipe, a vertical trench profile was successfully etched, and the profile was further improved by increasing the number of cycles from one to seven.

Next, we developed the recipe exploration method based on machine learning of feature data related to the etching profile in order to accelerate the optimization. A micro/macro cavity method is used to extract the feature data. An approximate region to obtain the vertical profile can be determined in the feature data space because the feature data show the characteristics of ion assist etching and radical etching. The relationship between the feature data and the recipes was learned, and feature data were then explored to obtain the vertical profiles. After the iteration of the exploration, it enabled us to determine the optimum recipes for the vertical profile in just seven times of Si trench etching.

[1] T. Ohmori et al., Proc. of Int. Symp. Dry Process, Tokyo, pp. 9–10 (2017).

[2] H. Nakada et al., Proc. Gaseous Electronics Conf., Pittsburgh (2017).

Plasma Science and Technology Division
Room 104C - Session PS+MN-WeM
IoT Session: Enabling IoT Era

Moderators: Ankur Agarwal, KLA-Tencor, David Lishan, Plasma-Therm LLC

8:00am **PS+MN-WeM1 A "Moore's Law" for Packaging***, **Subramanian Iyer**,* University of California at Los Angeles **INVITED**

While Silicon has scaled aggressively by over a factor of a few thousand over the last six decades the progress in packaging has been more modest – a linear factor 4-5 in most cases. In this talk, we will examine the reasons for this lag and what we are doing to fix this imbalance. Packaging is undergoing a renaissance where chip-to-chip interconnects can approach the densities of on-chip interconnects. We will discuss the technologies that are making this happen and how these can change our thinking on architecture and future manufacturing. Specifically, we will discuss two embodiments: Silicon as the next generation packaging substrate, and Flexible electronics using fan-out wafer level processing. We will describe how this is needed for the IoT era.

8:40am **PS+MN-WeM3 Fabrication, Chemical Lift-Off and Optical Characterization of Nanoscale III-Nitride Light Emitters***, **Lesley Chan**[1], C.D. Pynn, P. Shapturenka, T. Margalith, S.P. DenBaars, M.J. Gordon,* University of California at Santa Barbara

High density, near eye, and flexible display technologies of the future will require efficient micro- and nanoscale pixels based on light emitting diodes (LEDs). Liquid-crystal displays (LCD) and organic LEDs are currently used or envisioned for these applications, but their efficiencies and lifetimes are low. Higher efficiency III-nitride materials are promising for such displays, but manufacturing and implementing sub-micron scale InGaN/GaN structures that emit at different wavelengths into devices is currently difficult. Moreover, flexible and curved display applications require substrate thinning or separating individual devices from their growth substrates for subsequent printing or pick-and-place onto alternate substrates.

In this talk, we present an easy and scalable fabrication and chemical lift-off method to create nanoscale InGaN LEDs, along with morphological and optical characterization of the resulting structures using photo- (PL) and cathodoluminescence (CL). Active and sacrificial multi-quantum well (MQW) layers were epitaxially grown on semipolar (20-21) GaN substrates using MOCVD and patterned into large mesas (4x4 mm^2) using photolithography and Cl_2/N_2 plasma etching. Mesas were 'flip-chip' bonded to sapphire and chemically released from the GaN growth substrate by photoelectrochemical (PEC) etching of the sacrificial MQW layer, leaving behind a 1-2 µm thick p-GaN/MQW/n-GaN device layer protected with Si_3N_4. Nano-LEDs (nLEDs) were then patterned on the thin film device layer using colloidal lithography and plasma etching, released using HF vapor, and suspended in water, resulting in a colloidal solution of InGaN nLEDs. LED geometry was tuned by adjusting the SiO_2 colloid mask size (500-2000 nm) and plasma processing, e.g., using an isotropic CF_4/Ar mask reduction etch and vertical GaN etch with Cl_2/N_2. Preliminary PL results show a five-fold increase in emission for on-wafer nLEDs compared to their planar (unpatterned) counterparts. The large PL enhancement is thought to be due to increases in both IQE and EQE resulting from relaxed strain (decreasing the quantum confined Stark effect) and enhanced light extraction from increased scattering and graded index effects (i.e., non-planar geometries), respectively. CL spectroscopy and imaging of individual nLEDs also revealed strong MQW emission after processing with peak wavelengths at 430 nm. This work suggests that the 'flip-chip' approach, combined with colloidal lithography and chemical release, is a viable route to solution processable, high efficiency nanoscale light emitters.

9:00am **PS+MN-WeM4 High Radical Flux, with Low Ion and Photon Flux, Plasma Source, for MEM'S Technology***, **Marc Segers**, Y. Pilloux, D. Lishan, S. FERRAND,* Plasma-Therm LLC

Micro-electromechanical system (MEMS) are main constituent of a variety of sensors, that include pressure and vibration sensors, accelerometers and gyroscopes, and radiation and temperature sensors. MEMS is a technology that could answer the IoT's requirements for sensors high sensitivity.

To be able to produce MEMS with lower cost and higher quality, different steeps are necessary with preventive treatment, like substrate cleaning or sacrificial photoresist removal, with plasma.

In this work, we introduce a unique inductively coupled downstream plasma source configuration to generate high density radical concentration, for a chemical action and surface activation, but without high ion and photon fluxes, in opposition with conventional inductively coupled plasmas.

Our plasma technology provides a unique process capability for ultimate surface preparation, removal of most difficult residues formed during semiconductor and MEMS processing. System features an innovative approach to "Inductive Coupling", introducing a proprietary plasma confinement technology that is capable of a quasi-full gas dissociation inside the discharge tube, at low RF power. Although the plasma discharge tubes are isolated from the treatment chamber, with a remote plasma design, they deliver a large concentration of free radicals. That "High Density Radical Flux" technology (HDRF®) has demonstrated concentration levels up to 1,000 times higher than conventional plasma sources. HDRF® provides a damage free processing, allowing cleaning of high aspect ratio structures, preventing collapsing or stiction free of membranes, and

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

activation of ultra-sensitive materials, that could be find in MEMS technology. Most of applications include Bosch polymer removal, low temperature photoresist stripping, descum and activation of ultrasensitive surfaces prior to bonding, like MEMS capsuling or shielding.

The low ion and photon exposure significantly reduces the opportunity for damage to sensitive layers. This inductive plasma arrangement prevents local heating and charging on the wafer. With that low local electrical potential, the HDRF® is efficient with 3D structures on the wafer (e.g. MEMS and other high AR features) where preventing ion shielding effects is important.

This work will first describe the **HDRF®** source and different advantages for MEMS processing. Second, several applications using the HDRF® technology will be discussed. These applications will include cleaning of 30:1 aspect ratio (AR) silicon vias, removal of sacrificial layers in MEMS structures, low temperature photoresist removal, and surface smoothing of Bosch generated sidewalls using micro-isotropic etching.

9:20am **PS+MN-WeM5 Use of Plasma in Advanced Packaging*, Michael Seddon,*** ON Semi **INVITED**

Advanced Packaging is critical for the continually evolving demands of IoT. As additional functionality is added to the final product, and as its form factor is reduced to further promote mobility and compatibility, the semiconductor package has become even more critical in the integration and overall success of the technology. Advanced IoT packaging is required to offer not only the reliably and protection required of the technology, but it needs to offer the solution with the lowest possible power usage, most efficient use of space and footprint, improved thermal performance, while at a low cost to the end customer. This presentation will discuss several uses of plasma in advanced packaging solutions to meet these demands in both improving the overall reliability performance as well as offering new technology solutions.

11:00am **PS+MN-WeM10 Low Temperature Plasmas in Nanotechnology Applications*, Meyya Meyyappan,*** NASA Ames Research Center **INVITED**

The versatility and low temperature processing capability has allowed the use of gas discharges in a variety of nanotechnology applications. This talk will provide an overview of our activities on the use of low temperature plasmas in printed electronics and also the growth of nanomaterials and application development. We have developed an atmospheric pressure plasma jet as an alternative to inkjet and aerosol printing to deposit nanomaterials on paper, plastic, metal foils and textiles etc. to enable flexible, printable electronics. This is a single-step process that does not require a follow-on annealing or sintering in order to get consolidated thin films as is customary with other techniques. The surface temperature is in the range of 20-80 deg C depending on the carrier gas used and the morphology of the film can be controlled by varying the carrier gas and other plasma parameters. Examples of printed materials and their applications will be discussed. The talk will also cover growth of vertical graphene or carbon nanowalls using PECVD on various substrates with interesting properties as well as carbon nanofibers for a variety of applications. The author thanks Ram Gandhiraman, Jessica Koehne, Mike Oye, Mehrdad Shaygan, Mark Rummeli and Jeong-soo Lee.

11:40am **PS+MN-WeM12 Gas Phase Synthesis of Pure III-V Semiconductor Nanoparticles from Bulk Metals by using Low Temperature Plasma*, Necip Berker Uner,*** *E. Thimsen,* Washington University in St. Louis

III-V semiconductors are an important class of optoelectronic materials with applications that cover a broad range of the spectrum. Nanoparticles of many of the III-V materials, such as GaAs, InP and InSb, have been synthesized successfully with colloidal methods. However, high quality colloidal syntheses of stibnide and nitride nanoparticles haven't been reported yet. In this work, we present a general gas phase synthesis route for pure nanocrystals of GaSb and GaN. The method relies on reacting aerosols of different metals with help of a low temperature plasma (LTP). Aerosols of Ga, Sb and gaseous nitrogen bearing species were used as precursors. First, the aerosols of the constituent metals were generated via evaporation and condensation. Then, these aerosols were sent into a tubular argon LTP reactor, which provides continuous in-flight processing. As demonstrated in a previous study [1], particles vaporize in the LTP, and the resulting vapor may lead to nucleation of new particles or to re-condensation on the remaining clusters. During the synthesis of the III-V nanomaterials, unipolar charging prevents agglomeration, therefore free-standing particles were produced. Synthesized particles were found to be crystalline and they were mixed on an atomic scale. The stoichiometry was adjusted by manipulating input aerosol concentrations and applied plasma power. Materials were characterized *ex-situ* via high resolution transmission electron microscopy, energy dispersive x-ray spectroscopy, electron-energy-loss spectroscopy, x-ray diffraction and inductively-coupled plasma optical emission spectroscopy. The presentation will provide the results obtained through the extensive characterization methods mentioned. Furthermore, capping the synthesized particles with surfactants, effects of post-etching on the material, and photoluminescent properties will be presented. Operation of the aerosol sources and the mechanism leading to the formation of the compound materials will also be discussed.

[1] N. B. Uner and E. Thimsen, "In-Flight Size Focusing of Aerosols by a Low Temperature Plasma," *J. Phys. Chem. C*, vol. 121, no. 23, pp. 12936–12944, Jun. 2017.

12:00pm **PS+MN-WeM13 Investigation of Fundamental Hydrocarbon Plasma Chemistry for Unraveling Film Deposition Processes on Nanomaterials*, Tara Van Surksum,*** *E.R. Fisher,* Colorado State University

Nanostructured materials have numerous desirable properties (e.g., electronic, optical, high surface area) making them useful for range of applications (e.g., catalysts, sensors). However, in some cases, mechanical properties of the materials are not well-suited for their intended environment. Plasma processing of nanomaterials presents an ideal route to modify bulk and surface properties and ultimately, fine tune these materials for desired applications. Hydrocarbon plasmas are often employed to deposit amorphous hydrocarbon films and have been utilized in conjunction with nanostructured materials to increase material hardness. To date, however, a lack of understanding of the fundamental interactions between the material and gas-phase hinders material development. Thus, we aim to elucidate how hydrocarbon plasma deposition processes are influenced by substrate morphology and chemistry, and conversely, how the material ultimately influences the gas-phase chemistry of the plasma.

Here, inductively-coupled hydrocarbon plasma systems (e.g., CH_4, C_2H_4) are investigated to elucidate the roles of gas-phase radicals and gas-surface interactions during film growth processes for flat (e.g., glass slides, Si wafers) and nanostructured (e.g., SnO_2, TiO_2, ZnO) substrates. Materials properties are also assessed to determine the influence of the plasma parameters on film quality. X-ray photoelectron spectroscopy confirms the deposition of amorphous hydrocarbon films on all substrates and scanning electron microscopy images show morphological differences between films deposited under different plasma conditions. Raman spectroscopy reveals that plasma processing creates oxygen vacancies in the TiO_2 lattice structure. Additionally, optical emission spectroscopy is utilized to determine relative species' densities and rotational and vibrational temperatures ($T_R$and T_V, respectively) for multiple species (e.g., CH, C_2). In CH_4 plasma systems, T_V(CH) ranges from ~2000 to ~4000 K under most plasma conditions, whereas T_R(CH) generally reaches values ranging from 1800 to 2800 K. Both values appear to correlate with system pressure and applied rf power. In some cases, the nanostructured substrates have a measurable effect on the gas-phase chemistry (e.g., presence of additional gas-phase species, elevated T_R(CH)), whereas in others, the substrate does not appreciably alter the gas-phase of the plasma. Collectively, these data help to unravel these complicated systems by providing valuable insight regarding possible mechanistic phenomena in hydrocarbon plasmas linked to film deposition on materials with complex architectures.

Surface Science Division
Room 203C - Session SS+HC-WeM
Catalytic Alloys: Understanding Heterogeneity

Moderators: April Jewell, Jet Propulsion Laboratory, Jean-Sabin McEwen, Washington State University

8:00am **SS+HC-WeM1 Toward Surface Science-informed Design of Bifunctional Deoxygenation Catalysts*, J. Will Medlin,*** University of Colorado Boulder **INVITED**

A major challenge for catalysis is controlling the selectivity for desired reactions of biomass-derived compounds, including selective removal of oxygen atoms. Surface-level studies have the potential to provide deep insights into catalytic reaction mechanisms for deoxygenation. Using single-crystal metal surfaces as model catalysts, the elementary steps associated with both selective and non-selective reaction pathways can be mapped out in significant detail. Surface science studies have also elucidated roles of the different metals within bimetallic catalysts for complex deoxygenation reactions. This presentation will focus on how insights from such model studies have been used to inform efforts to design catalysts for deoxygenation and other key reactions of biomass-derived compounds. It will also discuss complications arising from the so-called pressure and materials "gaps" associated with the use of model surfaces, as well as opportunities for addressing these apparent limitations.

8:40am **SS+HC-WeM3 Computationally Assisted Correlative STEM and EXAFS Characterization for Multiscale Structure Determination of Tunable Rh/Au Bimetallic Nanoparticle Catalysts***, S. House, C.S. Bonifacio,* University of Pittsburgh*; J. Timoshenko,* Stony Brook University*; P. Kunal, H. Wan, Z. Duan, H. Li,* University of Texas at Austin*; **Judith Yang,*** University of Pittsburgh*; A.I. Frenkel,* Stony Brook University*; S. Humphrey, R. Crooks, G. Henkelman,* University of Texas at Austin

The acceleration of rational catalyst design by computational simulations is only practical if the theoretical structures identified can be synthesized and experimentally verified. Bimetallic catalysts have the potential to exceed the selectivity and efficiency of a single-component system but adding a second metal greatly increases the complexity of the system. Additionally, variation in the elements' mixing patterns and reconfiguration can affect the reaction mechanisms and thus catalytic performance [1]. Most experimental tools for the characterization of nanoparticles (NPs) provide structural data at the relevant length scales, but not enough to unambiguously determine the structure. Here we present our correlative theory-experiment design approach for addressing this issue, through application to the complex structures of Rh/Au bimetallic hydrogenation catalysts. Our calculations predict this system to exhibit superior allyl alcohol hydrogenation performance compared to single-element catalysts due to the ability to tune the hydrogen binding on the surface [2]. In this study, Rh/Au bimetallic NPs of different metal mixing ratios were synthesized via microwave heating and characterized using synchrotron extended X-ray absorption fine structure (EXAFS) spectroscopy and scanning transmission electron microscopy (STEM). EXAFS samples particle ensembles to extract information about atomic bonding (coordination, bond distances, etc.). TEM provides direct local characterization, down to the atomic scale, of particle size, morphology, and elemental distribution. The conventional approach to interpreting EXAFS – fitting to bulk reference spectra – is problematic for bimetallic NPs. We overcome this by using the STEM data to inform the generation of metal NP structures, calculated using interatomic potentials under the frame work the modified embedded-atom method (MEAM). EXAFS spectra for these structures were simulated and compared against the experimental EXAFS to iteratively refine the models, producing more atomic structures that were consistent with all experimental data, and will be more accurate for subsequent theoretical calculations. This work demonstrates that correlating the local characterization of TEM with the many-particle information from EXAFS grants a multiscale understanding not achievable with either approach alone.

[1] R. Ferrando, J. Jellinek, R.L. Johnston, Chem. Rev. **108** (2008), p. 845-910.

[2] S. Garcia, *et al.*, ACS Nano **8** (2014), p. 11512-11521.

9:00am **SS+HC-WeM4 Designing Heterogeneous Alloy Catalysts from First Principles and Surface Science***, **Charles Sykes,*** Tufts University

In this talk I will discuss a new class of metallic alloy catalysts called *Single Atom Alloys* in which precious, reactive metals are utilized at the ultimate limit of efficiency.[1-5] These catalysts were discovered by combining atomic-scale scanning probes with more traditional approaches to study surface-catalyzed chemical reactions. This research provided links between the atomic scale surface structure and reactivity which are key to understanding and ultimately controlling important catalytic processes. Over the last five years the concepts derived from our surface science and theoretical calculations have been used to design *Single Atom Alloy* nanoparticle catalysts that can perform industrially relevant reactions at realistic reaction conditions. For example, alloying elements like platinum and palladium with cheaper, less reactive host metals like copper enables 1) dramatic cost savings in catalyst manufacture, 2) more selective chemical reactions, 3) reduced susceptibility to CO poisoning, and 4) higher resistance to deactivation by coking. I go on to describe very recent theory work by collaborators Stamatakis and Michaelides at UCL that predicts reactivity trends of 16 different *Single Atom Alloy* combinations for important reaction steps like activation of H-H, C-H, N-H, O-H and C=O bonds. This project illustrates that the field of surface science is now at the point where it plays a critical role in the design of new heterogeneous catalysts.

References:

[1] Kyriakou et al. Science **335**, 1209 (2012).

[2] Marcinkowski et al. Nature Materials **12**, 523 (2013).

[3] Lucci et al. Nature Communications **6**, 8550 (2015).

[4] Liu et al. JACS **138**, 6396 (2016).

[5] Marcinkowski et al. Nature Chemistry **10**, 325 (2018).

9:20am **SS+HC-WeM5 Extracting Diffusing Parameters for Cu and S from Surface Segregation Data Recorded with AES on a Ni-Cu(S) Ternary Alloy***, **Jacobus Terblans,*** University of the Free State, South Africa*; X.-L. Yan,* University of the Free State, China*; J.Y. Wand,* Shantou University, China*; H.C. Swart,* University of the Free State, Republic of South Africa

The catalytic selectivity and activity of Cu-Ni bimetallic catalysts, used for oil hydrogenation, have been investigated extensively over the years. A catalytic surface that is Cu rich have higher selectivity than a Ni rich surface. The Cu-Ni alloy system has a simple phase diagram and forms a solid solution in the entire compositional range. In this study the segregation of Cu and S to the surface of a Cu-Ni alloy with 21.3 at.% Cu and 7 ppm S was measured by using Auger electron spectroscopy (AES) coupled with a linear programmed heater. It was found that first the Cu segregated to the surface and reached a maximum surface coverage of 40 %. Once the Cu reached a maximum surface coverage, it started to desegregate as it was replaced by the S that was also segregating to the surface. The measured segregation data were fitted by Fick's and Guttmann's ternary segregation models and the diffusing parameters (namely segregation energy (ΔG), interaction parameter (Ω), pre-exponential factor (D_0) and the diffusion activation energy (Q)) for both Cu and S were extracted from the data.

9:40am **SS+HC-WeM6 Atomic and Electronic Structure of CoO Nanoislands on Au(111)***, **Ana Sanchez-Grande,*** IMDEA Nanoscience, Spain*; J. Rodriguez-Fernandez,* Aarhus University, Denmark*; E. Carrasco, B. Cirera, K. Lauwaet,* IMDEA Nanoscience, Spain*; J. Fester,* Aarhus University, Denmark*; R. Miranda,* Universidad Autonoma Madrid, Spain*; J.V. Lauritsen,* Aarhus University, Denmark*; D. Ecija,* IMDEA Nanoscience, Spain

Oxides have found applications in various problems in the fields of chemistry, physics and materials science, notably for use in catalysis, encouraging investigation of fundamental properties of oxides. Hereby, transition metal oxides have been proposed as promising catalysts in the oxygen evolution reaction for water splitting, of crucial relevance in clean energy. Equipped with state-of-the-art scanning probe and sample-average techniques, atomistic insights for FeO [1] and CoO [2], [3] and their activity towards water splitting have been recently reported.

Despite this activity, there is a lack of knowledge about the precise atomic and electronic structure of most of these oxides. To understand better the activity of such catalysts, we have selected CoO nanoislands as an archetype model catalyst for water splitting. Our results show the complex atomic and electronic structure of CoO islands on Au(111), revealing the emergence of a Moiré pattern within the nanoislands. Such nanostructures show a higher density of states in the conduction band at the top moirons inside the nanoislands, while present an increase of the valence band states at the borders of the islands and at the bottom moirons inside the nanoislands. Importantly, oxygen dislocation lines induce profound electronic changes in adjacent regions (beta regions) within the nanoislands.

The exposure of such catalyst to water highlights that activity towards water splitting depends on substrate temperature. At room temperature [3], the water is adsorbed and dissociated, affording the formation of hydroxyls, which are located predominantly at the bottom moirons. However, at low temperatures the water is adsorbed intact exclusively on the beta regions and can be manipulated with the STM tip, affording a multi-level electronic molecular nano-switch.

Our results shed light into the atomistic adsorption and dissociation of water on a very promising catalysts and reveal that such a process is temperature dependent.

References:

[1]: Parkinson, G. S., Novotný, Z., Jacobson, P., Schmid, M. and Diebold, U. J. Am. Chem. Soc., **133** (32), 12650-12655 (2011).

[2]: Fester, J., García-Melchor, M., Walton, A. S., Bajdich, M., Li, Z., Lammich, L. and Lauritsen, J. V. Nat commun, **8**, 14169 (2017).

[3]: Walton, A. S., Fester, J., Bajdich, M., Arman, M. A., Osiecki, J., Knudsen, J. and Lauritsen, J. V. Acs Nano, **9** (3), 2445-2453 (2015).

11:00am **SS+HC-WeM10 Using Water as a Co-catalyst in Heterogeneous Catalysis to Improve Activity and Selectivity*, Lars Grabow,*** University of Houston **INVITED**

"What happens when you add water?" is possibly the most frequently asked question after presentations in heterogeneous catalysis. In this talk, I will demonstrate that this question is indeed paramount and that the presence of even minute amounts of water can drastically change reaction rates and product selectivities. Examples include water-mediated proton hopping across a metal-oxide surface, oxidation of carbon monoxide at the gold/titania interface, and hydrodeoxygenation of phenolic compounds over titania supported ruthenium catalysts. Together, these examples demonstrate that water can act as co-catalyst in a variety of catalytic reactions and by varying the amount of water it may be possible to tune reaction rates and product selectivity.

11:40am **SS+HC-WeM12 Experimental and Theoretical Evaluation of Water Chemistry on Two-dimensional Silica and Aluminosilicate*, Jin-Hao Jhang,*** *G.S. Hutchings,* Yale University*; J.A. Boscoboinik,* Center for Functional Nanomaterials Brookhaven National Laboratory*; E.I. Altman,* Yale University

The participation of water in zeolites is widely seen in catalysis, ion-exchange, and wastewater treatment. Water adsorption, dissociation and desorption all play critical roles in forming catalytically active Brønsted and Lewis acid sites. Recently, two-dimensional (2D) silica and aluminosilicate bilayers were fabricated on different substrates successfully. Prior studies have suggested that protonated 2D aluminosilicate can be formed and these protonated sites may be analogous to those in acid zeolites. Thereby, the 2D aluminosilicate shows its potential as a zeolite model. In this work, we studied water chemistry on 2D silica and aluminosilicate grown on a Pd(111) substrate by combining density function theory (DFT), thermal desorption spectroscopy (TDS), and ambient pressure photoelectron spectroscopy (AP-PES). We found that protonated 2D aluminosilicate on Pd(111) is thermally stable with both dehydrogenation and dehydration of the protonated surface energetically infeasible under 1000 K. Based on the theoretical and experimental results, once the aluminosilicate surface is protonated, no further water dissociation will take place. The AP-PES study suggests that molecular water can penetrates through the 2D bilayers and stays at the bilayer-substrate interface, leading to core-level shifts in the 2D bilayers due to changes of dipole moments. These findings show that the Brønsted acid sites on the Pd-supported 2D aluminosilicate are robust, and thereby provide fundamental information on the more complex zeolite surfaces.

12:00pm **SS+HC-WeM13 Double Layer Formation of Water Molecules on Graphene***, A. Akaishi, T. Yonemaru,* ***Jun Nakamura,*** The University of Electro-Communications (UEC-Tokyo), Japan

While graphite is known as hydrophobic material, recent studies have revealed that pristine graphitic surfaces are more likely to be hydrophilic. Hydrophobic/hydrophilic nature is closely related to wettability of surfaces. One of the characteristic measures of wettability is a contact angle that is the angle of the edges of a water droplet placed on target surfaces. It has been reported that the contact angle of water on graphite surfaces decreases as hydrocarbons on the surface are removed [1,2]. The contact angle estimated by molecular dynamics (MD) simulations, however, varies depending on a choice of the parameters of interaction potentials between a water molecule and graphitic surfaces [3]. On the other hand, water molecules have been confirmed to form layered structures on a graphene surface [4] and on the surface of carbon nanotubes [5]. But, the wettability of pristine graphene surfaces remains unsettled.

To investigate the water wettability of graphitic surfaces, we use molecular dynamics simulations of water molecules on the surface of a single graphene layer at room temperature [6]. The results indicate that a water droplet spreads over the entire surface and that a double-layer structure of water molecules forms on the surface, which means that wetting of graphitic surfaces is possible, but only by two layers of water molecules. No further water layers can cohere to the double-layer structure, but the formation of three-dimensional clusters of liquid water is confirmed. The surface of the double-layer structure acts as a hydrophobic surface. Such peculiar behavior of water molecules can be reasonably explained by the formation of hydrogen bonds: The hydrogen bonds of the interfacial water molecules form between the first two layers and also within each layer. This hydrogen-bond network is confined within the double layer, which means that no "dangling hydrogen bonds" appear on the surface of the double-layer structure. This formation of hydrogen bonds stabilizes the double-layer structure and makes its surface hydrophobic. Thus, the numerical simulations indicate that a graphene surface is perfectly wettable on the atomic scale and becomes hydrophobic once it is covered by this double layer of water molecules.

[1] Z. Li *et al.*, Nat. Mater. **12**, 925 (2013)

[2] A. Kozbial *et al.*, Carbon **74**, 218 (2014)

[3] T. Werder, J. H. Walther, R. L. Jaffe, T. Halicioglu, and P. Koumoutsakos, J. Chem. Phys. B **107**, 1345 (2003)

[4] Y. Maekawa, K. Sasaoka, and T. Yamamoto, Jpn. J. Appl. Phys. **57**, 035102 (2018)

[5] Y. Homma *et al.*, Phys. Rev. Lett. **110**, 157402 (2013)

[6] A. Akaishi, T. Yonemaru, and J. Nakamura, ACS Omega **2**, 2184 (2017)

Thin Films Division
Room 102A - Session TF+EM+MI-WeM
Thin Film Processes for Electronics and Optics I

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

8:00am **TF+EM+MI-WeM1 Crystalline Conductors: Transition Metal Nitride Materials and Device Applications*, David Meyer,*** *D.S. Katzer, N. Nepal, B.P. Downey, M.T. Hardy, D.F. Storm,* U.S. Naval Research Laboratory **INVITED**

Development of gallium nitride and related III-N materials thin film growth technology has been instrumental in realizing high performance light-emitting, RF, and power electronic devices for both commercial and military applications. To continue pushing the frontiers of nitride materials research, we have recently incorporated a multi-pocket electron-beam evaporator into our nitride molecular beam epitaxy growth system to enable the evaporation of refractory transition metals. In spite of the complexity of the equilibrium phase diagrams of transition metal nitide (TMN) compounds, we have found that it is possible to grow single-phase TMN thin films epitaxially on SiC and AlN by carefully managing growth kinetics. This talk will discuss our latest results involving TMNs, such as NbN_x and TaN_x, which can be nearly lattice-matched and integrated within III-N heterostructures. Cross-sectional transmission electron microscopy indicates that TMN/III-N interfaces are atomically abrupt with no evidence of interdiffusion of the host elements. We anticipate that the device applications of these metallic films are quite broad ranging from selective etching of sacrificial layers for epitaxial lift-off of processed devices, to buried metallic or superconducting electrodes for quantum computation circuit elements, to optical mirrors and waveguides for improved optoelectronics.

8:40am **TF+EM+MI-WeM3 Growth Mechanism and Characteristics of Hf-Si-O Film by PE-ALD using TDMAS and TDMAH Precursors and Oxygen Plasma Gas*, Toshihide Nabatame,*** National Institute for Materials Science (NIMS), Japan*; M. Inoue,* National Institute for Materials Science (NIMS)*; E. Maeda, K. Yuge, M. Hirose,* Shibaura Institute of Technology, Japan*; M. Takahashi, K. Ito,* Joining and Welding Research Institute, Osaka University, Japan*; N. Ikeda,* National Institute for Materials Science (NIMS), Japan*; T. Ohishi,* Shibaura Institute of Technology, Japan*; A. Ohi,* National Institute for Materials Science (NIMS), Japan

GaN-based power devices with metal-oxide-semiconductor (MOS) structure have been widely investigated for next-generation power devices. To reduce the leakage current, Hf-Si-O has one candidate material among various gate insulators. To fabricate Hf-Si-O film, a HfO_2/SiO_2 laminate film was generally deposited by ALD. The growth mechanism of SiO_2 films was greatly changed by the oxidant gas when Tris(dimethylamino)silane (TDMAS) was as precursor [1]. By using ozone gas, the stable growth rate and high quality SiO_2 films could be obtained while no growth using H_2O gas. We expect that similar data can be also obtained by using oxygen plasma gas. However, the growth mechanism of the SiO_2 film during HfO_2/SiO_2 laminate film deposition and its characteristics have not been fully understood.

In this study, we systematically investigate growth rate of HfO_2/SiO_2 laminate film by plasma-enhanced ALD (PE-ALD) using TDMAS and Tetrakis(dimethylamino)hafnium (TDMAH) precursors and oxygen plasma gas, and also examine characteristics of the Hf-Si-O films.

The HfO_2/SiO_2 laminate films were deposited on SiO_2/Si substrates by PE-ALD at 300 °C with TDMAH and TDMAS precursors and oxygen plasma gas. The composition Hf/Si ratio of the HfO_2/SiO_2 laminate films were varied by changing each number of ALD cycle. The SiO_2 film was also deposited on SiO_2/Si and HfO_2/Si substrates by the same PE-ALD condition. The Hf-Si-O films were formed by post-deposition annealing (PDA) at 700 – 900 °C in a N_2 atmosphere. The growth per cycle (GPC) of the HfO_2/SiO_2 laminate, HfO_2, and SiO_2 films was estimated by spectroscopic ellipsometry, XPS, and cross-sectional TEM measurements. The structure of Hf-Si-O films was identified by XRD analysis, and electrical characteristics of capacitors with Hf-Si-O films were examined using capacitance – voltage measurement.

The GPC of the HfO_2/SiO_2 laminate, HfO_2, and SiO_2 films on SiO_2/Si substrates were found to be 0.08, 0.08, and 0.04 nm/cycle, respectively, regardless of Hf/Si composition ratio. Considering to the GPC of the HfO_2 (0.08 nm/cycle), the estimated GPC of a SiO_2 layer during HfO_2/SiO_2 laminate film deposition was 0.08 nm/cycle, which was unexpected, but increased by about 2 times compared to that of SiO_2 film on SiO_2/Si substrate. This suggest that an initial adsorption of TDMAS precursor on the SiO_2 and HfO_2 films must be different and strongly affects to the GPC. The Hf-Si-O films (Hf/Si=2/1) maintains amorphous structure even after PDA temperature at 900 °C. The Hf-Si-O films (Hf/Si=2/1) exhibited high dielectric constant of around 14 as expected.

Reference

[1] L. Han, and Z. Chen, ECS J. of Solid Sate Sci. and Technol., 2 N228 (2013).

9:00am **TF+EM+MI-WeM4 Atomic Layer Epitaxy of Ultra-wide Bandgap Ga_2O_3 Films**, ***Virginia Wheeler***, *N. Nepal,* U.S. Naval Research Laboratory*; L.O. Nyakiti,* Texas A&M University*; D.R. Boris, S.G. Walton, B.P. Downey, D.J. Meyer,* U.S. Naval Research Laboratory*; C.R. Eddy, Jr.,* U. S. Naval Research Laboratory

Ga_2O_3 has emerged as a promising material for next generation power electronics and UV photodetectors applications due to its large bandgap (4.9 eV) and the availability of affordable native substrates from melt-grown bulk crystals. While β-Ga_2O_3 (monoclinic) is the most stable and studied of five polymorphs, the slightly less energetically favorable α- and ε-Ga_2O_3 phases have unique characteristics that can be exploited. The α-Ga_2O_3 (rhombohedral corundum) has the largest bandgap of 5.3 eV and can be alloyed with α-Al_2O_3 and α-In_2O_3 for bandgap engineering. T he ε-Ga_2O_3 phase (hexagonal wurtzite) is a polar phase, with a calculated polarization strength that is 10 and 3 times larger than that of GaN and AlN, respectively. Like the III-N system, polarization induced charges can lead to higher charge densities and mobilities in two-dimensional electron gases formed at heterojunctions, which would improve the viability of Ga_2O_3 electronic devices. In this work, we use atomic layer epitaxy (ALEp) to produce high-quality homo- and heteroepitaxial Ga_2O_3 films and investigate phase selectivity as a function of substrate type and orientation, growth temperature (T_g), plasma gas phase chemistry and gas pressure.

All ALE Ga_2O_3 films were deposited in a Veeco Fiji G2 reactor equipped with a load lock and turbo pump using trimethygallium and O_2 plasma precursors. Initial studies on c-plane sapphire substrates showed that decreasing chamber pressure an order of magnitude during the plasma step resulted in a shift from pure β-Ga_2O_3 to pure α-Ga_2O_3. Additionally, at 350°C and 8 mTorr, the phase could be altered by a varying the O_2 plasma flow from 5-100 sccm. Optical emission spectroscopy indicate that the ratio of O*/O2 is critical for phase selectivity while the high ion flux to the surface can contribute to the crystallinity at low T_g. By varying T_g from 300 to 500°C at 8 mTorr, films went from mixed β/ε phase at <350°C, to pure α-Ga_2O_3 at 350°C, to pure β-Ga_2O_3 at 500°C. Using the optimum growth conditions for α-Ga_2O_3 on c-sapphire, the influence of substrate was explored using a variety of substrates including AlN, GaN (bulk and epilayers), SiC, diamond, and Si. Deposition on III-N and β-Ga_2O_3 substrates all resulted in crystalline β- Ga_2O_3 films, while amorphous films were deposited on both SiC and Si. This suggests that a clean crystalline substrate interface is critical to obtaining high quality films and promoting metastable phases is more dependent on growth parameters than underlying crystal symmetry. Finally, we will discuss simple electrical properties of optimum films of each phase to validate feasibility of the process in device applications.

9:20am **TF+EM+MI-WeM5 Effects of Process Gases and Gate TiN Electrode during the Post Deposition Anneal to ALD-Al_2O_3 Dielectric Film**, ***Masaya Saito***, *A. Teramoto, T. Suwa, K. Nagumo, Y. Shiba, R. Kuroda, S. Sugawa,* Tohoku University, Japan

We investigated effects of a post deposition anneal(PDA) to Al_2O_3 film which was formed by the low temperature atomic layer deposition(ALD)(1). Al_2O_3 films were formed at 75°C by the ALD process using $Al(CH_3)_3$ as a precursor and H_2O as an oxidant, and these thicknesses were 40 nm. TiN films were formed as gate electrodes of MIS capacitors. We applied three kinds of PDAs. N_2 and O_2 annealing at 400°C were applied just after the ALD(PDA Ⅰ(a), (b)), and N_2 annealing at 400°C was applied after the gate electrode formation (PDA Ⅱ). We measured C-V and I-V characteristics.

The negative V_{FB} compared to the ideal one(+0.54 V) was observed in the C-V curve without PDAs, and the fixed charge density calculated from V_{FB} was ~10^{13} cm^{-2}. In contrast, positive V_{FB} compared to the ideal one was observed in the C-V curve with PDA Ⅰ(b), and the fixed charge density was ~10^{11} cm^{-2}. These results indicate that PDA Ⅰ(b) is effective to decrease the fixed charges. Moreover, the hysteresis in the C-V curve decreased by PDA Ⅰ(b), and the leakage current also decreased within the voltage range of C-V measurement. It is considered that the decrease of hysteresis was caused by decreasing the electrons that were trapped in the Al_2O_3 film(2). However, a few samples broke down at low voltage after PDA Ⅰ(b). In contrast, we couldn't measure the C-V characteristics of almost capacitors with PDA Ⅰ(a) because the capacitors broke down at low voltage. In the case of PDA Ⅱ, which means N_2 annealing after the gate electrode formation, the leakage current decreased same as PDA Ⅰ(b) and the production yield was still good even after PDA Ⅱ This was different tendency from PDA Ⅰ(a) even as the same annealing. However, V_{FB} shifted to the positive voltage by the PDA Ⅱ, and the fixed charge density was ~10^{12} cm^{-2}. This was the same phenomenon as the PDA Ⅰ(b).

We considered these phenomena as follows; the oxidizing species were desorbed by PDA just after the ALD, and then the film quality was bad after the N_2 annealing. The oxygen for improving the film was supplied by the O_2 annealing with the desorption. When PDA was carried out after the gate electrode formation, the desorption did not occur because of capping by the gate electrode, and then the oxidizing species were sufficient for improving the film by the annealing.

Reference:

(1) Y. Koda, et al., *ECS Trans.*, **72**(4), 91-100 (2016)

(2) L. Sambuco Salomone, et al., *J. Appl, Phys.*, **123**, 085304 (2018)

Acknowledgement:

This work was carried out at fluctuation free facility of New Industry Creation Hatchery Center, Tohoku University.

9:40am **TF+EM+MI-WeM6 Controlling the NbO_xMaterials System for Neuromorphic Computing**, ***Alexander C. Kozen***, U.S. Naval Research Laboratory*; Z.R. Robinson, A.H. Rowley,* The College at Brockport - SUNY*; T.J. Larrabee, M.E. Twigg, H.S. Cho, S.M. Prokes,* U.S. Naval Research Laboratory

The niobium oxide system has seen recent interest, particularly due to its potential use as both a non-volatile, in the case of Nb_2O_5, or volatile, in the case of NbO_2, memristor material. Nb_2O_5 is a high k dielectric (k~41) with a high refractive index (n~2.2) and a wide bandgap (3.5 eV), while NbO_2 is a thermochromic material with a lower bandgap (1.2 eV) that undergoes a first order crystalline phase transition at a critical temperature (T_c) of 800˚C. Both of these phases, along with their intermediate sub-oxides, can serve as material components of memristors to facilitate low-power neural computing hardware.

We will examine the impact of annealing temperature, duration, and atmospheric chemistry on the phase selectivity of the NbO_x thin films fabricated using atomic layer deposition. Anneals of stoichiometric amorphous Nb_2O_5 films are kinetically limited by both Nb^{5+} to Nb^{4+} reduction and crystallization steps, and we find that the addition of H_2 during annealing is critical for the Nb^{5+} to Nb^{4+} reduction. To remove this kinetic-limiting step, we instead deposit reduced amorphous NbO_2 films, which crystallize at lower temperatures. We investigate the optical and electrical properties of both amorphous and crystalline NbO_x films and discuss the utility of the NbO_x materials system to the fabrication of memristor materials.

11:00am **TF+EM+MI-WeM10 Sputtering Power Dependent on Switching Characteristics of ZnO-based Transparent Resistive Memory Devices**, ***Firman Mangasa Simanjuntak***, Tohoku University, Japan*; T. Ohno,* Oita University, Japan*; S. Samukawa,* Tohoku University, Japan

Transparent resistive random access memory (T-RRAM) devices have great potential as data storage for invisible electronics.[1] ZnO material is one of the promising candidates for T-RRAM application due to its high transparency to the visible light.[2] However, ZnO is an *n*-type semiconducting material which the intrinsic donor defects exist abundantly; consequently, the ZnO-based switching devices require high current compliance to operate as compared to another oxide system .[1,3] The employment of the high current compliance is to facilitate the formation of conducting filament. Various efforts have been made to improve the ZnO-based switching memories, such as: by controlling the thickness, introducing a dopant(s), adjusting the gas ambient during deposition, stacking with various material(s) and structure(s).[1] However, modulating the switching characteristics by controlling the sputtering power is still less overlooked. In this work, we investigated the influence of sputtering power in resistive switching characteristics of ZnO-based T-RRAM devices.

An approximately 50 nm thickness of ZnO films were deposited onto Indium Tin Oxide (ITO)-coated transparent substrates using conventional RF sputtering. Various sputtering power was used for the deposition while Ar/O_2 ambient is maintained at 2/1 ratio. The deposition rate was measured using a surface profilometer. In order to fabricate sandwich device structure, circular gallium-doped ZnO (GZO) top electrodes were deposited onto the ZnO/ITO structure; patterned using a metal shadow mask with 150 µm in diameter. X-ray diffraction and X-ray photoelectron spectroscopy were used to investigate the crystal structure and the defect concentration of the ZnO films, respectively. A semiconductor device analyzer was used to measure the electrical characteristics of the devices.

XRD pattern indicated that all ZnO films show (002) oriented crystals. The devices made with higher sputtering power showed lower leakage current for OFF state and lowered current compliance to form the conducting filament (for ON state). We also found that the donor defects (oxygen vacancies and zinc interstitials) decrease as the sputtering power increases. These findings indicate that the sputtering power parameter cannot be simply overlooked in the T-RRAM fabrication.

References

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11:20am **TF+EM+MI-WeM11 Influence of Iintrinsic and Extrinsic Dopants in HfO_x Films for Resistive Switching Memory**, ***SungYeon Ryu**, Y. Kim,* Seoul National University of Science and Technology, Republic of Korea; *W.Y. Park, S.G. Kim,* SK Hynix Inc., Republic of Korea; *B.J. Choi,* Seoul National University of Science and Technology, Republic of Korea

Bipolar type resistive switching random access memories (RRAMs) utilized by TaO_x and HfO_x as switching materials, have been demonstrated superior to unipolar type RRAMs owing to the low switching current and better reliability. Bias-polarity-dependent valence change mechanism in HfO_x is attributed to the repeated generation and rupture of conducting filaments (CF), which could be the clusters of oxygen vacancies (V_o). As the device size scales down to 2x nm, the dimension of CF and the whole device area become comparable, and thus the involvement of oxygen loss or unintended V_O incorporation, that is, intrinsic defects may significantly degrade the device reliability. On the other hand, extrinsic defects by doping metallic elements may also change the switching characteristics and device variability depending on the fabrication methods, such as, co-sputtering, implantation, thermal and photo-assisted diffusion, etc.

In this study, influence of both intrinsic and extrinsic defects was investigated systematically. The device having TiN contact-plug with 28 to 2000-nm-diamenter formed in SiO_2 inter-layer was fabricated. 1.2-nm-thick HfO_x layer was deposited by atomic layer deposition (ALD). At first, for the control of intrinsic defect, the fabricated RRAM devices were post-annealed in both air and vacuum (~10mTorr) at a wafer temperature of 150 to 250 ^{o}C for 20 min, respectively. Electrical property is measured by semiconductor parameter analyzer (HP-4155) and function generator (AFG-3102) for DC and AC measurements. More reliable switching and free-from abnormal switching behavior, such as reset-failure, were observed in the vacuum-annealed device.

Secondly, Al- and Ga-doped HfO_x films are grown by using thermal ALD to change the structural and chemical properties of HfO_2 film via incorporating extrinsic defects. Dopant concentration and location were controlled by the ALD cycle ratio and sequence. Through Al doping, pristine resistance and forming voltage of the device were increased with increasing Al cycle ratio. On the other hand, Ga-doped HfO_2 device showed reverse switching polarity. The resistive switching characteristics caused by intrinsic and extrinsic defects in HfO_x films will be presented in detail.

Acknowledgment

This paper was result of the research project supported by SK hynix Inc.

11:40am **TF+EM+MI-WeM12 Scaling up of an Electrochemical Atomic Layer Deposition of Copper**, *D. Dictus,* Lam Research Corporation, Belgium; ***Aniruddha Joi**,* Lam Research Corporation; *G. Alessio Verni,* Lam Research Corporation, Belgium; *K. Vandersmissen,* Imec, Belgium; *B. Frees,* Lam Research Corporation, Belgium; *Y. Yezdi,* Lam Research Corporation

Just like atomic layer deposition in the gas phase, electrochemical atomic layer deposition in the liquid phase holds the promise of delivering very good conformality and uniformity for nm-thick film deposition by using surface limited reactions. Up to today however, there is no industry in which such process has been scaled up from cm-size coupons to industrial-scale substrates. In this paper, the scale up of electrochemical ALD of Cu is reported and it is demonstrated that this process can be used to fill <20 nm Cu interconnect lines as required for future microchip technology nodes.

The e-ALD process is a cyclic process that consists of a step in which a monolayer of Zn is deposited at a potential below the one, at which, Zn would grow multilayers (underpotential deposition), followed by a step in which the zinc is spontaneously displaced by Cu when the substrate is allowed to drift to the open circuit potential (surface limited replacement reaction, SLRR). By cycling between potentiostatic Zn deposition and open-circuit steps, Cu films can be grown in layer-by-layer fashion.

In contrast to classical electroplating processes, e-ALD processes do not require significant overpotential to create uniform nucleation. Also, current densities are small since the deposited amount of material per cycle is low. Therefore, the e-ALD process can be used to deposit Cu with atomic layer thickness control on substrates with high resistivity which gives the advantage of being able to plate on very thin (sub-20 A) liner materials.

Development of the e-ALD process is done on a Sabre electroplating tool from Lam Research on 300 mm substrates. These substrates contain a thin layer of Ru or Co on which the copper is deposited. The e-ALD process forms the seed layer for further metallization of the interconnect or can by itself fill the narrow interconnect lines.

We will demonstrate that good thickness uniformity can be achieved on 300 mm substrates with initial sheet resistance up to 1000 Ohm/sq and that filling of interconnect lines with dimensions smaller than 14 nm is achieved. Test chips containing our new Cu deposition process show high yield and the Cu interconnect lines have low resistance. This demonstrates the potential use of this new production method in future technology nodes.

12:00pm **TF+EM+MI-WeM13 A Novel High-deposition-rate PECVD Process based on Hollow Cathode Plasma Technique**, *S. Shayestehaminzadeh, N. Rivolta,* AGC Glass Europe, Belgium; *M. Datz,* Interpane E&B GmbH; ***John Chambers**,* AGC North America; *H. Wiame,* AGC Glass Europe, Belgium

AGC Plasma has recently developed a hollow cathode plasma device as part of its activity as the industrial vacuum equipment manufacturing segment of AGC. This device has been successfully scaled up in order to perform the Plasma Enhanced Chemical Vapor Deposition (PECVD) processes for the coatings on the glass sizes ranging from a few square-centimeters up to a few square-meters (jumbo-sized glass plates 3.2 x 6.0 m^2). Plasma generation is undergone between multiple linear hollow cathode cavities, alternately driven by commercially available mid-frequency AC or pulsed power. This enables the generation of a dense and uniform plasma inside the cavities as well as outside of the cavities through the linearly located holes where a less dense plasma (as compared to inside the cavity) but still dense enough, can be utilized in order to activate the reaction between precursor and reactive gases in the depositing chambers. This geometry and condition allow the system to be scalable to relevant sizes for any typical vacuum processes.

The selected plasma generation method does not require magnets incorporated into the source. This will allow a simplified cooling system within the plasma source, as well as the possibility for adding other magnets to be positioned within the process chamber for modifying the plasma geometry. Based on plasma and vacuum simulations, the electrode-cavity design has been dramatically improved and can be driven by various gases, such as oxygen, nitrogen, argon, helium, and hydrogen. Plasma operation is also possible in an extremely wide range of pressures from 1 mTorr to 1 Torr, while the most useful process pressures for PECVD are generally in the 1 mTorr to 30 mTorr range. The wide hollow cathode pressure operation range allows for the deposition of multilayer coating stacks by magnetron sputtering and PECVD in the same vacuum coating lines.

Electrode faces have also been enhanced using surface coatings to avoid erosion during high power operation, also reducing subsequent debris and extending source lifetime. Depending on the choice of precursor materials, the desired film properties, and in-chamber magnetic field geometries, dynamic deposition rates for inline PECVD coatings of 200-500 nm*m/min have been demonstrated for SiO_2 on flat glass products however by selecting different gases and precursors various materials can be deposited using the same source line. This unique process opens a new range of possibilities to be investigated for a variety of substrates. These plasma sources are now commercially available in either lab or industrial sizes to explore new applications.

Vacuum Technology Division
Room 203B - Session VT-WeM

Vacuum Technology Developments

Moderators: Jason Carter, Argonne National Laboratory, Yulin Li, Cornell University

8:00am **VT-WeM1 Trace Helium Effects from High Pressure Swing Adsorption Nitrogen Generator on Semiconductor Capital Equipment Manufacturer***, **William Johnson**,* Applied Materials, Varian Semiconductor Equipment

A High Pressure N2 Pressure Swing Adsorption (HPN PSA) N2 generator was installed to replace the three LN2 bulk storage tanks on the AMAT VSE campus. An Ion Implanter has many multi-stage roots, exhaust lines and turbomolecular pumps that use GN2 as a purge gas. It was found that He introduced by the PSA GN2 generator was of sufficient quantity to raise the background level of many devices under test to the 10^{-6}sccs range, desensitizing the leak testing processes. This work will describe the basic PSA N2 generation process, the methods by which errant He entered the process and the method used to alleviate the excess He.

8:20am **VT-WeM2 Remote Handling Clamps for Flange Connections in Vacuum Service***, **Ryan McCall**,* Technetics Group

Sealing a vacuum connection remotely in a hostile or radioactive environment can present a difficult challenge for scientists and engineers. This critical application requires easy assembly and disassembly of the flange connection while reducing the number of individual components that must be handled. The QDS or Quick Disconnect System uses a contiguous chain clamp mechanism with two conical flanges and a customized seal that eliminates the need for loose bolts and nuts. In addition, the clamp connection can be fitted to a guide plate that ensures the clamp is always properly aligned. The QDS is of all metal construction and utilizes a spring energized metal seal to provide Helium leak rate performance with little or no permeation or outgassing. Typically, the QDS will require less space than a bolted flange and often requires less torque to create a tight seal.

9:00am **VT-WeM4 Role of Rotor Surface Conditions on Calibration Constant of Spinning Rotor Gauges***, **Tim Verbovsek**,* Institute of Metals and Technology, Slovenia

In spinning rotor gauges, measured pressure is inversely proportional to the tangential momentum accommodation coefficient (TMAC), a quantity which is affected by interactions between gas molecules and the rotor surface. This is why control over surface conditions of the rotor is extremely important, in order to accurately determine pressure. In our study, surface of rotor spheres were altered by various treatment steps, and changes in the TMAC with respect to the initial condition. For this purpose three different treatment steps were taken, each done over 24 hours. First the rotor sphere was vacuum baked at 300 °C. Next, the rotor sphere was heated again at 300 °C in oxygen at 1e-2 Pa. Finally, it was heated at 300 °C in pure hydrogen at 1e-2 Pa. In order to examine reproducibility of the method, two rotor spheres were simultaneously treated, while one rotor sphere was used as a control. TMAC of the untreated spheres and after each treatment step was determined using primary static expansion calibration system which was developed at Institute of Metals and Technology. Additionally, in order to determine the dependence of TMAC on the gas used, measurements were repeated for six pure gases; helium, methane, neon, nitrogen, argon and krypton. Results obtained showed a relative change in TMAC of up to 7% after heating in oxygen. Furthermore, a strong dependence on the gas used was observed, where largest change of the TMAC was observed for helium and neon.

9:20am **VT-WeM5 Condensation-based Low-grade Heat Powered Dual-chamber Vacuum Technology***, **Tony Guo**,* New Jersey Institute of Technology

Vacuum processing technologies are widely used in general industrial applications. Most of the current vacuum technologies such as positive displacement pumps, momentum transfer pumps, entrapment pumps and ejectors have to rely on electricity and /or compressor as the prime power source to generate the vacuum. Our technology provides an economic method to generate the vacuum by only using low-grade energy like waste heat, realized by steam condensation mechanism and dual-action piston-cylinder design. Our vacuum system is composed of 4 parts: one actuator-vacuum generation pump, where steam will be filled into and condensed to generate the vacuum environment; one extracting pump, deliver the vacuuming process, driven by the actuator through a linear connected piston; one boiler, to supply the steam to actuator as the prime energy source; an application chamber, connected with the extracting pump, to evaluate the vacuuming performance.

A system design of our technology will be presented and the vacuuming process will be demonstrated by 3D animation. A lab-scale prototype will be demoed via photos and video. The dynamic process of vacuuming for both actuator and driven pump has been mathematic modeled via MATLAB. For model correction, the tricky problems in the process, such as gas leakage and discharge, have been studied via CFD.

Key words: vacuum generation, low grade heat utilize, dynamic process model, CFD

9:40am **VT-WeM6 Vacuum Design and Testing of the ARIEL Radio Frequency Quadrupole Buncher and Cooler (ARQB)***, **Geoff Hodgson**, B. Barquest,* TRIUMF, Canada

The ARQB is an installation on the RIB (Radioactive Ion Beam) beamline in the new ARIEL (Advanced Radioactive IsotopE Laboratory) facility. The ARQB accepts continuous radioactive beam from future proton and electron-excited targets in the basement of ARIEL, and from existing targets in TRIUMF's ISAC facility. The buncher creates 10 to 100 Hz bunches for injection into the EBIS (Electron Beam Ion Source) for charge breeding. The ARQB is held at roughly +60 kV to electrostatically deaccelerate the beam to 150 keV at the injection optics. Between the ARQB and the EBIS, is a pulsed drift tube that reduces the ground potential beam energy to roughly 15 keV.

The cooling and bunching takes place in the core of the buncher in 0.05 mbar and ~80K helium. Helium is supplied through a stepper-controlled variable leak valve. Cooling is provided by a cryocooler thermally bonded to a copper jacket around the quadrupole core. The quadrupole electrodes and support structures create a differential pumping barrier between the core and the body of the ARQB chamber, which is expected to be held at 7e-4 mbar with one turbo pump. The injection and extraction electrodes create a second layer of differential pumping volumes, where pressure is expected to be 5e-5 mbar.

The design is based on the BECOLA beam cooler and buncher at Michigan State University. Vacuum testing is expected to start May 2018, and first stable isotope beam injected in October 2018. First radioactive beam from ISAC is expected in early 2019, and first beam from the ARIEL target in 2021.

Wednesday Morning, October 24, 2018

Exhibitor Technology Spotlight Workshops
Room Hall A - Session EW-WeB

Exhibitor Technology Spotlight Session IV

Moderator: Christopher Moffitt, Kratos Analytical Inc

10:20am **EW-WeB2 HAXPES-Lab: A Laboratory Based System for HAXPES Measurements*, Susanna Eriksson,*** Scienta Omicron

Scienta Omicron's HAXPES-Lab brings hard X-ray photoelectron spectroscopy (HAXPES) capability directly to the end user's laboratory. This novel system enables the investigation of buried interfaces, in-operando devices and real world samples, all without the need for a synchrotron end station. By combining a state-of-the-art, monochromized 9.25keV Ga X-ray source with the proven Scienta Omicron wide acceptance angle hemispherical analyzer, the HAXPES-Lab sets the standard for laboratory based high energy photoelectron spectroscopy.

10:40am **EW-WeB3 Coatings Characterization Solution from Fischer Technology - XRF, Nanoindentation and Progressive Load Scratch*, Rahul Nair,*** Fischer Scientific

This talk discusses the key features that aid in increased productivity and usability of the Fischer's non-destructive coating thickness (XRF) and mechanical (nanoindentation and scratch) testers. Fischer is a pioneer in the field of nanoindentation (since 1985) and XRF (since 19XX). The standard measurement and computation of coating thickness and mechanical properties are performed in accordance to ISO and ASTM standards with minimal influence by the operator. Fischer's primary focus has been on reduced measuring time and higher throughput while producing accurate and precise measurements. Some of the key features in our nanoindentation and scratch testers that aid this are single-step tests, programmable test cycles, significantly reduced time to detect surface, improved autofocus, graphical presentations and automated report generation. Additionally, because of the high resolutions for load and distance the Fischer instruments can be used for a broad range of applications and materials. It is even possible to determine the plastic and elastic material properties of even very hard and thin coatings.

Exhibitor Technology Spotlight Workshops
Room Hall A - Session EW-WeL

Exhibitor Technology Spotlight Session V

Moderator: Christopher Moffitt, Kratos Analytical Inc

12:40pm **EW-WeL3 The TESLA JT SPM***, Markus Maier,* Scienta Omicron GmbH, Germany

The TESLA JT SPM provides access to more than 5 days SPM measurement time at temperatures down to 1K (4He

operation) with magnetic fields larger than B > 3T. Careful thermal design of the bath cryostat and JT cooling stage

as well as the integrated UHV magnet lead to exceptionally low LHe consumption of only 11 liters LHe for 120

hours, specifically also during magnet operation and field variation. The external JT Helium supply allows for 3He

operation and significantly lower temperatures in the range of 500mK.

The microscope head is a proven, highly stable design developed specifically for high magnetic field environments.

It offers the full range of SPM measurements modes, including Scienta Omicron's leading QPlus AFM technology.

Safe and independent tip/sample exchange under optical control is one of several key ease-of-use features delivering

dependable high performance SPM and successful scientific work.

In contrast to a conventional wet magnet concept, the dry split-pair magnet provides for optical access enabling

various optical experiments and even in-situ evaporation into the SPM at low temperatures.

We will discuss the technical concept and will show performance evaluation measurements at T=1K that prove

stability below 1pm as well as energy resolution on superconductors.

Specifically, continuous STM and QPlus AFM imaging at varying temperatures during magnetic field ramping

without increasing the LHe consumption differentiate the concept from traditional 4He and 3He systems and open

up new experimental possibilities.

1:00pm **EW-WeL4 MKS Instruments, Inc., 523 Granville-Phillips® Wide-Range Cold Cathode Transducer: Applications and Market Update***, David Kelly,* MKS Instruments

A dual-discharge, wide-range cold cathode ionization gauge, marketed by MKS Instruments, Inc. as the 523 Granville-Phillips® Wide-Range Cold Cathode Transducer, was commercially disclosed at the Exhibitor Technology Spotlight session one year ago. This novel technology promised unprecedented low-cost of ownership for industrial vacuum applications requiring limited pressure measurement accuracy between atmosphere and 10^-7 Torr.

Several facilities have now tested the technology and vacuum technologists all over the world are quickly experiencing first-hand the unique capabilities of this revolutionary technology. This presentation describes several examples of real-world applications of the new product with a focus on process compatibility, sensor lifetime, and overall cost-reductions experienced by customers in manufacturing, research facilities and general vacuum applications, who are seeking alternative pressure measurement capabilities. The initial voice-of-customer reports confirm the original performance and cost features and benefits assertions originally stated by MKS Instruments.

2D Materials Focus Topic
Room 201B - Session 2D+MN+NS+SS-WeA

IoT Session: Surface Chemistry, Functionalization, Bio and Sensor Applications

Moderator: Daniel Walkup, National Institute of Standards and Technology (NIST)/ University of Maryland, College Park

2:20pm **2D+MN+NS+SS-WeA1 Impact of Hydrogen on Graphene-based Materials: Atomistic Modeling and Simulation of HRSTEM Images***, C. Guedj,* Univ. Grenoble Alpes, CEA, LETI, France*; L. Jaillet, F. Rousse,* ***Stéphane Redon,*** Univ. Grenoble Alpes, CNRS, INRIA, Grenoble INP*, LJK, France

The hydrogen energy transition is highly probable, because hydrogen is the most abundant element in the universe and represents an ideal “green” source of energy. Meanwhile, the safe hydrogen production and storage remains a major challenge still in progress. Potential production and storage materials include graphene. In terms of electronic and optoelectronic applications, hydrogen can tune the bandgap of graphene [1]. Hydrogen also plays a major role during the Chemical Vapour Decomposition (CVD) growth of graphene [2]. Hence, hydrogenated graphene-based materials are potentially relevant for various technological applications.

To understand and optimize the device efficiency and the interface engineering, it is advantageous to perform advanced nanocharacterizations, linked to numerical modelling and simulations. This task is particularly difficult, because hydrogen is labile and prone to rapid reorganization. This structural evolution may be monitored with transmission electron microscopy (TEM) techniques [3,4,5], but in spite of significant progresses, the direct detection of hydrogen with High Resolution Scanning Transmission Electron Microscopy (HRSTEM) or energy-loss spectroscopy still remains a serious challenge.

We investigate here the interaction of hydrogen with graphene using the Brenner module of the SAMSON software platform https://www.samson-connect.net and we propose an original methodology to characterize its structural arrangement at the atomic scale by simulating HRSTEM images to interpret experimental results. In particular, we compare the effect of hydrogen on dark field (DF), bright field (BF), high-angle annular dark filed (HAADF) and annular bright field (ABF) images, to estimate the best technique suited to hydrogen detection.

In addition, we present the effect of carbon vacancies and adatoms on the stability of hydrogen coverage, associated to the HRSTEM signatures of the most stable configurations. These results provide the necessary building blocks to analyze the structure and energetics of hydrogenated graphene-based materials at the atomic scale.

References

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2:40pm **2D+MN+NS+SS-WeA2 High Density H2 and He Plasmas: Can They be used to Treat Graphene?***,* ***Hasan-Al Mehedi,*** Laboratoire des Technologies de la Microélectronique, CNRS-UJF, France*; D. Ferrah,* Cea, Leti, Minatec, France*; J. Dubois, C. Petit-Etienne,* Laboratoire des Technologies de la Microélectronique, CNRS-UJF*; H. Okuno,* Cea, Inac/sp2m/lemma*; V. Bouchiat,* Institut Néel, CNRS-UJF-INP*; O.J. Renault,* CEA/LETI-University Grenoble Alpes, France*; G. Cunge,* Laboratoire des Technologies de la Microélectronique, CNRS-UJF, France

Since graphene and other 2D materials have no bulk, a major issue is their sensitivity to surface contaminations, and the development of cleaning processes is mandatory. High density plasmas are attractive to treat (clean, dope, pattern) 2D materials because they are a mature industrial technology adapted to large area wafer. However, in these plasmas the substrate is bombarded by a high flux of both thermal radicals and reactive ions with typical energy above 10 eV, which can easily damage atomic layer thin materials. We have investigated systematically the interaction of H2 and He inductively coupled plasmas (ICP) with graphene in industrial reactors. We report a specific issue associated with the use of H2 plasma: they etch the inner part of plasma reactor walls, thus releasing impurities in the plasma, most notably O atoms that etch graphene and Si atoms which stick on it. The presence of parasitic oxygen presumably explains the discrepancies found in the literature regarding the impact of reactive plasmas on graphene damages. To get rid of this issue we propose to use a fluorinated aluminum chamber. In this case, fluorine atoms which are shown to be harmless to graphene are the only impurity in the plasma. Under such conditions H2 ICP plasma is shown to clean graphene without damages if the ion energy is kept below about 15 eV.

3:00pm **2D+MN+NS+SS-WeA3 Novel Binder-free Ag@Ni(OH)₂ over Graphene/Ni Foam and Glucose Sensing***,* ***Tong-Hyun Kang,*** *J.-S. Yu,* DGIST, Republic of Korea

Graphene combining with metal nanoparticles or other compounds is widely recognized to be a viable strategy to assemble high-activity catalysts.Unique properties of high conductivity and transparency, 2D morphology, and high stability in acid and alkaline solutions make graphene an excellent electron transfer medium on the interface of graphene/active materials as catalysts.Among them, graphene/metal nanoparticle (G/MNP) composites have been attracting more interest because of remarkably enhanced catalytic property, which is ascribed to a synergic effect from the interface of graphene and active sites. In general, reducing agents and electrodeposition methodshave been employed to *in-situ* reduce metal ions such as Au^{3+}, Pt^{4+}, Ag^{+}, and Cu^{2+} (M^{x+}) to MNPs on the graphene to form G/MNP composites.In this study, graphene is grown on nickel foam (NF) by chemical vapor deposition (CVD), which is directly used for MNP deposition. Different from bare NF, special phenomenon is observed that the graphene-coated nickel foam (GNF) composite can greatly speed up the electrodeless reduction of M^{x+} ions on the surface of the graphene. Interestingly, the MNP deposition and $Ni(OH)_2$ nanosheet assembly simultaneously occur on the GNF. Binder-free $Ni(OH)_2$-wrapped Ag hybrid developed on the GNF (Ag@$Ni(OH)_2$-GNF) is found to serve as an efficient electrochemical sensor because of its unique structure. A low detection limit of 0.3 μM and high sensitivity are achieved for the glucose detection, which confirms that the hierarchical electrode structure of Ag@$Ni(OH)_2$-GNF composite is highly effective to have extensive applications.

3:20pm **2D+MN+NS+SS-WeA4 Surface Modification and Magnetization of Carbon Based Nanostructures***,* ***Rina Tannenbaum,*** University of Stony Brook*; I.T. Kim,* Gachon University, Korea*; S. Sharma,* University of Stony Brook

We describe here a novel synthesis for the facile decoration of carbon nanomaterials (CNM) with monodisperse γ-Fe_2O_3 magnetic nanoparticles. These procedures were developed for multi-walled carbon nanotubes (MWNTs), reduce graphene (rGO) and reduced graphene nanoroses (rGO-roses). The decoration of these carbon nanomaterials with γ-Fe_2O_3 induces the magnetization of these structures and opens up the potential for their use in novel applications.

CNM/γ-Fe_2O_3 magnetic nanostructures were fabricated through a modified sol-gel process using ferric nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$ as a starting material. Nucleation sites for the iron oxide were generated at the CNM surface due to the electrostatic interaction between Fe (III) ions and the carboxylate surface groups of acid-treated CNMs. The occurrence of gelation was inhibited by the addition of the NaDDBS surfactant, before the addition of propylene oxide, which is a gel promoter. The surfactant interfered in the growth stage of the iron oxide nanoparticles (gel phase) through to the coordinaton of the NaDDBS molecules to the iron (III) centers due to the attraction between the negatively-charged hydrophilic head of the surfactant and the positively-charged iron. The rGO-roses were further fabricated from decorated rGO via a novel emulsion process.

Various characterization methods were used to confirm the formation of well-defined maghemite nanoparticles, and show that they were tethered to the walls of the CNMs. The tethered γ-Fe_2O_3 nanoparticles imparted magnetic characteristics to the CNMs, which in turn, became superparamagnetic. The magnetic carbon nanotubes and magnetic rGO were introduced into a polymer matrix [#] and were oriented parallel to the direction of an externally-applied magnetic field. The anisotropic nanocomposites were then used as anodes in lithium ion batteries. The magnetic rGO-roses were used as nuclear magnetic resonance contrast material.

4:20pm **2D+MN+NS+SS-WeA7 Chemical Modification of Graphene and Carbon Nano Tubes as viewed by XPS and NEXAFS Spectroscopies underpinned by DFT Spectra Simulation***, C. Ehlert, E. Donskyi,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany*; P.L. Girard-Lauriault,* McGill University, Canada*; R. Illgen,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany*; A. Lippitz,* Bundesanstalt für Materialforschung und -prüfung (BAM)*; R. Haag, M. Adeli,* Freie Universität Berlin, Germany*; **Wolfgang Unger**,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany

Graphene is a two-dimensional carbon network with unique properties. However, its low solubility, poor reactivity and the limited accessibility of a well-defined basal plane are major challenges for applications. An ideal method to overcome these problems is the covalent attachment of functional molecules to its surface which enable further reactive modifications for specific applications. There are several technologies for surface functionalization of graphene and related CNT materials. To get control on the functionalization process and to optimize the performance of the modified surfaces analytical tools for surface chemical characterization are required. X-ray absorption (NEXAFS) and photoelectron spectroscopy (XPS) have been identified to be rather powerful here [1-3]. Specifically, NEXAFS spectroscopy underpinned by quantum chemical spectrum simulations [4] is unique in a way to address changes of aromaticity and defect formation at the graphene surface during functionalization.

For relevant surface modification technologies, we present examples on how NEXAFS and XPS are fit for purpose. All presented modifications aim on the production of platforms for defined functional 2D nanomaterials, as for example multi-functional hybrid architectures. In detail we investigated:

- A wet chemical method for covalent functionalization of graphene sheets by a one-pot nitrene [2+1] cycloaddition reaction under mild conditions. Here a reaction between 2,4,6-trichloro-1,3,5-triazine and sodium azide with thermally reduced graphene oxide (TRGO) results in defined dichlorotriazine-functionalized graphene sheets.
- Graphene and carbon nanotube functionalized by Vacuum-Ultraviolet (VUV) induced photochemical or r.f. cw low pressure plasma processes to introduce amino, hydroxy or brominated functionalities.

To underpin finger-print information delivered by C K-edge NEXAFS we studied the effects of selected point and line defects as well as chemical modifications for a single graphene layer model by density functional theory based spectrum simulations.

Acknowledgement

We acknowledge support by the team at the BESSY II synchrotron radiation facility in Berlin, Germany, as well as Dr. A. Nefedov (Karlsruhe Institute of Technology, KIT) from the HE-SGM Collaborate Research Group.

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4:40pm **2D+MN+NS+SS-WeA8 Elastic Spongy Graphene-Functionalized Silicon Anode with Excellent Cycle Stability in Li battery***, **Byong-June Lee**, J.-S. Yu,* DGIST, Republic of Korea

Graphite plays a prominent role as a typical anode material in the lithium ion batteries (LIBs) because of its high lithiation-dilithiation reversibility and low voltage window. Unfortunately, the capacity is limited to 372 mAh g^{-1}[1,2]. To search for materials with higher lithium storage capacity, a great number of investigations on metal oxides (or sulfides), Sn, P, and Si have been carried out in recent decades. Among these materials, silicon can make alloy with lithium in the form of $Li_{22}Si_5$ to deliver a highest theoretical gravimetric capacity of ~4200 mAh g^{-1}, and thus is considered to be one of the most promising anode materials for next generation LIB. It is worth mentioning that its quite low delithiation potential and high lithium storage capacity can provide a wide working voltage window and energy density, which enable promising potential application in electric vehicles. However, those advantages are seriously offset by a great challenge of large volume expansion during lithiation process and the resultant breakage of bulk silicon particles and solid electrolyte interface (SEI), which causes a serious damage to the electrode structure and thus gives rise to a fast decay of the specific capacity [3].

In this work, novel 3D spongy grapheme (SG)-functionalized silicon is for the first time demonstrated by chemical vapor deposition for a LIB anode, which can overcome the common silicon anode issues such as poor conductivity and volume expansion of Si as well as transfer of Li ion towards the Si. The elastic feature of graphene has excellent function to self-adaptively buffer the volume variation during charge-discharge process. In particular, different from traditional graphene or carbon shells (core-shell and yolk-shell), the spongy 3D graphene networks provide much improved unique functions with excellent long-cycle stability and rate capability. The Si@SG electrode exhibits excellent cycling performance with high reversible specific capacity [4]. A superior 95% capacity retention is achieved after 510 cycles. All the electrochemical performances get benefits from the well-designed functional SG shells, where interconnected nano-graphene structure not only guarantees a high conductive network but also provides more free paths for excellent mass transfer in addition to self-adaptive buffering capability .

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5:00pm **2D+MN+NS+SS-WeA9 Electrical and Structural Changes of Multilayer WSe_2 Transistors: Atmospheric Gas Adsorption and Long Term Aging***, **Anna Hoffman**, M.G. Stanford, C. Zhng,* University of Tennessee Knoxville*; I. Ivanon,* Oak Ridge National Laboratory*; A.D. Oyedele, D.G. Mandrus,* University of Tennessee Knoxville*; L. Liang, B.G. Sumpter, K. Xiao,* Oak Ridge National Laboratory*; P.D. Rack,* University of Tennessee Knoxville

Interest in transition metal dichalcogenides (TMDs) for opto-electronic applications has been growing recently due to their unique properties and layered structure. Surface science and DFT simulations have corroborated p-type doping and n-type suppression of O_2 and H_2O adsorption in TMDs however, electrical characterization has not been fully investigated. This presentation will demonstrate the reversible suppression of n-type conduction in ambi-polar WSe_2 via water adsorption, which logically has a larger impact as the WSe_2 thickness decreases. Additionally, we observe a reversible and irreversible n-type suppression and p-type doping which we attribute to H_2O adsorption and isoelectronic oxygen chemisorption, respectively, at chalcogen vacancies during long term aging in atmosphere over 6 weeks. Finally, controlled oxygen plasma exposure is utilized to oxidize and p-type dope WSe_2. We will overview our device fabrication and electrical testing procedure, and transfer characteristics for our as-fabricated devices for various WSe_2 thicknesses in air and in vacuum will be illustrated. Long-term (6 week) electrical measurements in both air and vacuum are compared to the as-fabricated devices. Finally, complementary atomic force microscopy and Raman Spectroscopy are used to characterize the devices

5:20pm **2D+MN+NS+SS-WeA10 Ion Migration Studies in Exfoliated 2D Molybdenum Oxide via Ionic Liquid Gating for Neuromorphic Device Applications***, **Cheng Zhang**, P.R. Pudasaini, A.D. Oyedele,* University of Tennessee Knoxville*; A.V. Ivelev, K. Xiao, T.Z. Ward,* Oak Ridge National Laboratory*; D.G. Mandrus,* University of Tennessee Knoxville*; O.S. Ovchinnikova,* Oak Ridge National Laboratory*; P.D. Rack,* University of Tennessee Knoxville

The formation of an electric double layer in ionic liquid (IL) can electrostatically induce charge carriers and/or intercalate ions in and out of the lattice which can trigger a large change of the electronic, optical and magnetic properties of materials and even modify the crystal structure. We present a systematic study of ionic liquid gating of exfoliated 2D molybdenum trioxide (MoO_3) devices and correlate the resultant electrical properties to the electrochemical doping via ion migration during the IL biasing process. A nearly nine orders of magnitude modulation of the MoO_3 conductivity is obtained for the two types of ionic liquids that are investigated. In addition, notably rapid on/off switching was realized through a lithium-containing ionic liquid whereas much slower modulation was induced via oxygen extraction/intercalation. Time-of-Flight Secondary Ion Mass Spectrometry confirms the Li intercalation. Results of short-pulse tests show the potential of these MoO_3 devices as neuromorphic computing elements due to their synaptic plasticity.

5:40pm **2D+MN+NS+SS-WeA11 Infrared Absorption of Nanometer-scale Thermally Reduced Graphene Oxide*, Erin Cleveland*,** *J. Nolde, G. Jernigan, E. Aifer,* U.S. Naval Research Laboratory

Strong optical absorption is of fundamental importance to infrared (IR) sensors, and it has been well established that graphene is one of the strongest IR absorbing materials, with approximately 2.3% absorption in the IR and visible regions for a single layer. While reduced graphene oxide (RGO) may not have quite the same absorption strength as graphene on a layer-by layer basis, we believe that by controllably reducing the oxygen concentration within the GO films we can increase the absorption of the RGO film to approach that of graphene. RGO films, unlike graphene, however, can be made arbitrarily thick, allowing for much higher absorbance in a single pass. Here we explore the use of GO films of varying thickness and UHV annealing temperature to achieve near 100% midwave IR absorbance in a quarter-wave reflection filter structure consisting of an RGO film on top of a $\lambda/4$-thick SiO_2 layer deposited over a Ti/Pd mirror.

Graphene oxide (GO) is a two-dimensional network consisting of a graphene basal plane decorated with oxygen moieties in the forms of carbonyls, epoxies and hydroxyl groups resulting in variable number of $sp^2$and sp^3bonding geometries. Theory indicates that GO bandstructure and transport are strongly dependent on the ratio of the sp^2 and sp^3 bonding fractions, and therefore, by controllably removing specific oxygen groups, one can tune its electronic, optical, and chemical properties. While it is difficult to modify the oxygen concentration using wet chemical processing, e.g. using hydrazine, GO can be thermally reduced in H_2-N_2 forming gas with more precise control. However, this procedure, like chemical reduction promotes the occurrence of N and H impurities, as well as carbon vacancies within the graphene basal plane, significantly degrading the electronic quality of the film. Here, we use ultrahigh vacuum ($<10^{-9}$ Torr) annealing to controllably reduce the oxygen concentration in GO films while introducing fewer defects. Not only does UHV annealing prevent the introduction of impurities, but after oxygen removal, dangling bonds tend to reform in hexagonal structure. UHV annealing also enables in-vacuo measurement by x-ray photoelectron spectroscopy (XPS) to precisely characterize the overall oxygen concentration and its distribution within alcohol, epoxy and carbonyl species. Following an 800°C UHV anneal for example, we find that the oxygen concentration is reduced to ~5%, and the layer spacing is equivalent to epitaxial graphene grown on the C-face of SiC.

6:00pm **2D+MN+NS+SS-WeA12 Dielectric Properties of Carbon Nanomembranes prepared from aromatic Self-Assembled Monolayers and their application in All-Carbon Capacitors*, Xianghui Zhang*,** *P. Penner, E. Marschewski,* Bielefeld University, Germany*; T. Weimann, P. Hinze,* Physikalisch-Technische Bundesanstalt, Braunschweig, Germany*; A. Gölzhäuser,* Bielefeld University, Germany

Carbon nanomembranes (CNMs) are two-dimensional materials that are made by cross-linking self-assembled monolayers (SAMs) of aromatic molecules via low energy electron irradiation. Previous studies of the charge transport in molecular junction incorporating SAMs and CNMs of oligophenyl thiols has been carried out by using conical eutectic Gallium-Indium (EGaIn) top-electrodes[1] and conductive probe atomic force microscopy (CP-AFM)[2]. Additional investigations of the dielectric properties of pristine SAMs and CNMs were performed by impedance spectroscopy on EGaIn tunneling junctions. Here we demonstrate the fabrication and characterization of all-carbon capacitors (ACCs) composed of multilayer stacks of dielectric CNMs that are sandwiched between two types of carbon-based conducting electrodes: (1) trilayer graphene made by chemical vapor deposition and mechanical stacking; (2) pyrolyzed graphitic carbon (PGC) made by pyrolysis of cross-linked aromatic molecules. The junction area is defined by the width of electrode ribbons, ranging from 1 to 2500 μm^2, and the separation between two electrodes is tuned by the number of CNM layers. The frequency response of nanocapacitors was measured with an LCR meter. A dielectric constant of 3.5 and a capacitance density of up to 0.5 $\mu F/cm^2$ were derived from the junction capacitance. A dielectric strength of 6.2 MV/cm was determined. These results show the potential of carbon nanomembranes to be used as dielectric components in next-generation environment-friendly carbon-based molecular electronic devices.

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Actinides and Rare Earths Focus Topic
Room 202C - Session AC+AS+SA-WeA

Chemistry and Physics of the Actinides and Rare Earths

Moderators: Krzysztof Gofryk, Idaho National Laboratory, Ladislav Havela, Charles University, Prague, Czech Republic, David Shuh, Lawrence Berkeley National Laboratory

3:00pm **AC+AS+SA-WeA3 Bond Distance Variations for Lanthanide and Actinide Compounds and its Implication*, Tsuyoshi Yaita,*** Japan Atomic Energy Agency, Japan*; S. Suzuki, T. Kobayashi, H. Shiwaku,* Materials Sciences Research Center, Japan Atomic Energy Agency, Japan **INVITED**

Lanthanide and actinide are f-electron filling series and the properties of the series on their chemical behavior are very similar if valence states are same, while an electronic configuration of the inner shell for each element is slightly different compared to the similarity in size, and the value of special elements such as Nd and Dy used as neodymium magnet is high in the use of high-tech products. Regarding actinides series, radiotoxic Am is paid for attention in the geological disposal of radioactive waste and the R&D for partitioning and transmutation technique is performed. Accordingly, intra-series separation for lanthanide and actinide with similarity in chemical behavior would be quite important for the recovery of noble metal used as high-tech parts and treatment of high-level waste prior to geological disposal, resulting that the development of useful separation system could improve economic efficiency and reduction of environmental load.

On these backgrounds, we focus on the intra-series separation for lanthanide and actinide, especially, the relationship between variation of separation efficiency in the series and systematics of structure and electronic structure, and then, we try to propose new separation concept. Especially, in this talk, we talk about the variation of hydration or complex bond distances for trivalent actinide and lanthanide series based on X-ray crystallography and EXAFS and the interpretation based on the SX-XAS/XES and theoretical calculation.

4:20pm **AC+AS+SA-WeA7 Spectroscopic Studies of Trivalent Actinide Coordination*, Benjamin Stein*,** *M.G. Kerlin, A.L. Morgenstern, E. Batista, S.E. Bone, S.K. Cary,* Los Alamos National Laboratory*; J. Lezama Pacheco,* SLAC National Accelerator Laboratory*; S.A. Kozimor, P. Yang,* Los Alamos National Laboratory **INVITED**

Radioisotopes have a rich history in medicine, with their use dating back to the earliest studies of radioactivity. Only recently, however, have α-particle emitting radionuclides been considered for medical applications. Targeted alpha therapy utilizes the unique properties of α-emitting radionuclides to selectively kill cancer cells, with the short range of α-particles causing minimal collateral damage to nearby healthy cells. Actinium-225 (^{225}Ac) has been identified by the Department of Energy Isotope Program Long Range plan as an isotope of high national interest for targeted alpha therapy, due to its favorable half-life (10 days) and 4 α-emissions in the decay chain. However, if the ^{225}Ac is not securely bound to the targeting vector this effectiveness results in very high toxicity to off-target (i.e. healthy) cells. Due to the high radioactivity and limited supply of all actinium isotopes, very little fundamental chemistry is known about this elusive element. Utilizing the unique radiological facilities at Los Alamos, we have been able to use microscopic amounts (~30 micrograms) of the longer-lived isotope actinium-227 (half-life of 22 years) for chemical studies. Utilizing this isotope, we have developed handling and containment techniques to perform "classic" spectroscopic and chemical studies in support of developing actinium chelates to advance the use of ^{225}Ac in targeted alpha therapy. During these studies of actinium coordination chemistry we have also made comparisons with the more "traditional" trivalent actinides, in particular americium and curium. We will discuss our latest EXAFS, NMR, and computational results on these difficult to handle elements by presenting a comparison of acetate and phosphonate binding, and how this informs chelator development.

5:00pm **AC+AS+SA-WeA9 Speciation of Rare Earth Elements in Coal Harvesting Byproducts*, Xu Feng*,** *M. Council-Troche, J.R. Morris, A. Noble, R.-H. Yoon,* Virginia Polytechnic Institute and State University

Rare earth elements (REEs) are critical for the development of renewable energy resources, national security, and advanced manufacturing. With the recent closure of the rare earth mine in California, the U.S. relies entirely on foreign imports mainly from China, which poses serious economical and national security concerns. According to a study commissioned by the National Energy Technology Laboratory (NETL), the U.S. coal and coal byproducts contain ~11 million metric tons of recoverable REEs, only a small fraction of which could satisfy the domestic need [1].

Recent USGS studies showed that the REEs in U.S. coals are preferentially partitioned to clay minerals [1], suggesting that the clay byproducts may be a major source of the critical materials. Ion-adsorbed REEs in clay appear to exist as two distinct forms: (1) ionic species adsorbed by coulombic attraction which is thought to be the primary form in REE-adsorbed clay deposits in South China, and (2) colloidal REEs formed by hydrolysis, each requiring a unique extraction strategy. However, the conditions under which the ion-exchange clays were formed in the U.S. coals and accompanying mineral matter may be different from those for the South China ion-adsorption clays, and the specific speciation of REEs in U.S. coal materials is currently unknown. It is, therefore, critical to study the fundamental mechanisms by which REEs are adsorbed on clay minerals in aqueous media to develop effective targeted extraction strategies.

In this work, X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical state of representative light and heavy rare earth elements on artificial REE-adsorbed clay samples. Characteristic REE $3d_{5/2}$ features of the artificial clay sample, including the peak position of the two multiplet-split components, the magnitude of the multiplet splitting and the intensity ratio of each multiplet-split component, were compared to those of the high-purity REE standards such as REE(OH)$_3$, REE$_2$O$_3$ and REECl$_3$ to provide insight into the identification of REE speciation on the artificial sample. XPS results suggest that REE(OH)$_3$ is the primary REE species on the artificial REE-adsorbed clays. Furthermore, X-ray Adsorption Spectroscopy (XAS) was used to probe the speciation of representative light and heavy REEs in natural coal and coal byproduct samples by comparing the oxidation states and specific bonding environments to those of REE standard materials.

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5:20pm **AC+AS+SA-WeA10 Exotic Electronic Properties of Strongly Correlated Compounds NpPd$_3$ and PuPd$_3$***, **Krzysztof Gofryk,*** Idaho National Laboratory*; J.-C. Griveau, E. Colineau,* Institute for Transuranium Elements*; K.A. McEwen,* University College London*; W.J. Nellis,* Harvard University*; J.L. Smith,* Los Alamos National Laboratory

Actinides are characterized by the coexistence of localized and itinerant (delocalized) 5*f*-states near the Fermi energy. This dual nature of the 5*f*-electrons leads to many complex phenomena that are observed in these strongly correlated materials, spanning magnetic ordering, heavy-fermion ground state, unconventional superconductivity, and/or "non-Fermi liquid" state. The electronic properties of the strongly correlated electron systems are related to the formation, near the Fermi level, of a narrow band with large density of states and in spite of intensive theoretical and experimental efforts their nature is still not well understood. This behavior is well emphasized in *An*Pd$_3$ (*An*-U, Np, Pu) system. UPd$_3$ crystalizes in the hexagonal crystal structure and shows four phase transitions below 7.8 K, attributed to a succession of antiferroquadrupolar orderings of the uranium ions localized on the quasi-cubic sites of the *d*hcp structure. Depending on a heat treatment, NpPd$_3$ crystalizes in hexagonal and cubic crystal structures. The hexagonal NpPd$_3$ (*h*-NpPd$_3$) exhibits two transitions at 30 and 10 K. It has been suggested that the low temperature transition might be due to ordinary antiferromagnetic ordering while the high temperature one might be caused by a quadrupolar order. The cubic NpPd$_3$ (*c*-NpPd$_3$) orders antiferromagnetically below 52 K and the magnetic and transport measurements suggests that the transition is first order. PuPd$_3$ crystalizes in the cubic structure and shows an antiferromagnetic order below 24 K. To explore the influence of electronic correlations on the physical properties in the *An*Pd$_3$ system, here we present our detailed magnetic, thermodynamic, and transport studies of NpPd$_3$ and PuPd$_3$.We show that all results obtained present characteristic behaviors of 4*f*- and 5*f*-electron strongly correlated materials. The magnitude and overall temperature dependence of the electrical resistivity, magnetostesitivity, Hall and Seebeck effect, and heat capacity of NpPd$_3$ and PuPd$_3$ are archetypal of materials with Kondo interactions. Our measurements also reveal an unusual magnetic ordering in *c*-NpPd$_3$. At T$_N$, the specific heat exhibits an extremely large peak [as large as 1000 J/(mol K)] and the magnetic susceptibility shows a clear jump. The transport properties of *c*-NpPd$_3$ indicate a dramatic reconstruction of the electronic structure at the Néel temperature, probably accompanied by a large change in the Fermi surface topology, which shows up as pronounced anomalies at this temperature in the electrical resistivity, the magnetoresistivity, and the Seebeck and the Hall coefficient. We will discuss implications of these results.

Extending Additive Manufacturing to the Atomic Scale Focus Topic
Room 102B - Session AM+MP+NS-WeA

Atomic Scale Manipulation with SPM

Moderator: Sven Rogge, University of New South Wales, Australia

2:20pm **AM+MP+NS-WeA1 Advanced Scanning Probe Lithography: Processes, Nanopatterning and Nanoelectronics***, **Ricardo Garcia,*** Inst Ciencia Materiales Madrid, CSIC, Spain **INVITED**

The nanoscale control afforded by scanning probe microscopes has prompted the development of a wide variety of scanning probe-based patterning methods. Some of these methods have demonstrated a high degree of robustness and patterning capabilities that are unmatched by other lithographic techniques. However, the limited throughput of scanning probe lithography has prevented their exploitation in technological applications. Here, we review the fundamentals of scanning probe lithography and its use in materials science and nanotechnology. We introduce several methods, interactions and/or processes such as chemical, mechanical or thermal that enable the tip to modify surfaces. In particular, the presentation is focused on describing the fundamentals and applications of oxidation SPL for nanopatterning and device fabrication of nanoscale field-effect transistors, quantum dots, biosensors and molecular architectures involving a variety of systems from 2D materials to biomolecules; from self-assembled monolayers to silicon.

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3:00pm **AM+MP+NS-WeA3 Integrated Devices made Using Atomically Precise Advanced Manufacturing***, D. Ward, D. Campbell, M. Marshall, T.-M. Lu, L. Tracy, L. Maurer, A. Baczweski, **Shashank Misra,*** Sandia National Laboratories

Atomically precise advanced manufacturing (APAM) has enjoyed considerable success in demonstrating high profile physics demonstrations, such as the single atom transistor. However, a considerably broader application space would open up if other transistor elements could be integrated with APAM devices, opening the door to high gain and room temperature operation. However, integration is generally limited by the high temperatures required to prepare pristine silicon substrates for APAM, and by the low temperatures at which phosphorus donors diffuse away once placed into silicon once APAM is complete. Here, we describe progress in integrating metal-dielectric surface gates to achieve high gain, and compensation doping to achieve room temperature operation. The Digital Electronics at the Atomic Limit (DEAL) project is supported by Sandia's Lab Directed Research and Development Program, and was performed in part at the Center for Integrated Nanotechnologies, a U.S. DOE Office of Basic Energy Sciences user facility. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

4:20pm **AM+MP+NS-WeA7 Electrical Transport Properties of Si:P δ-layer Devices***, **Ranjit Kashid,** X. Wang, Namboodiri, J. Hagmann,* National Institute of Standards and Technology (NIST)*; S.W. Schmucker,* University of Maryland College Park*; J. Wyrick, C. Richter, R.M. Silver,* National Institute of Standards and Technology (NIST)

Si:P has been realized as one of the ideal systems for donor-based quantum computation. Site-selective doping of phosphorous atoms at the atomic scale using Scanning Tunneling Microscopy (STM) lithography on the Si(100) 2×1:H surface enables the fabrication of these devices. In the past, our group has demonstrated that degenerately doped & well confined Si:P monolayers can be fabricated using phosphine dosing and low-temperature Molecular Beam Epitaxy (MBE). In addition, a wide range of

1D and 2D nanoscale devices can be fabricated by combining STM lithography and low-temperature MBE. Here, we present magnetotransport and low-frequency 1/f noise measurements on degenerately doped 1D nanowires, 2D Hall Bars, and van der Pauw structures defined using STM lithography. Specifically, we investigate the dephasing mechanism and present a comparative analysis of transport between STM patterned and mesa etched Si:P δ-layer van der Pauw structures to further elucidate the effects of STM patterning on transport properties.

4:40pm **AM+MP+NS-WeA8 Atomically Precise Tip Positioning for Automated Writing of Atomic-scale Devices***, **James Owen**, E. Fuchs, J.N. Randall, J.R. Von Ehr,* Zyvex Labs

Hydrogen depassivation lithography has enabled unprecedented sub-nanometer precision in the positioning of dopant atoms in silicon,[1] advancing the field of silicon quantum electronics. It has also been used for localised atomic layer deposition of Si [2] and TiO_2[3].

In pursuit of our overall vision of Atomically Precise Manufacturing, we are pursuing a number of tactics towards automated fabrication of atomically precise structures. STM lithography vectors are automatically aligned to the surface atomic lattice, and patterns can be input as geometric shapes or arbitrary bitmaps. To improve tip position precision, we have developed real-time creep and hysteresis error correction. Using this, we have previously demonstrated open-loop atomic precision patterning over length scales up to 100 nm. Above this scale, where hysteresis errors are more significant, we are able to reduce the position errors by ~90%.

In parallel with real-time position corrections, we have developed automatic fiducial alignment routines. The tip position can either be aligned to previously-drawn patterns or to deliberate fiducial marks. A large pattern can therefore be stitched together from write fields within which atomic precision can be obtained. Thus, precise patterning can be scaled to large areas.

In the burgeoning field of Quantum Metamaterials[4], large arrays of single dopant atoms are required, with extreme position precision and very high yield. However, the yield of the current thermal process for P limits the yield to 70%[5].

Based on recent work on removal of H from surface PH_2 species[6], we are developing a tip-assisted incorporation process, which prevents the recombination and desorption process. For this application, we need to write single-dimer patterns to adsorb only one PH_3 molecule. For these small patterns, Automated Feedback Controlled Lithography is used, so as to remove exactly the required H atoms from the surface. We are working to improve the detection of the H atom removal, using not only the spike in tunnel current but also the change in the local barrier height [7].

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5:00pm **AM+MP+NS-WeA9 Kilobyte Scale Data Storage through Autonomous Atom Assembly***, A.F. Otte, **David Coffey**,* Delft University of Technology, Netherlands **INVITED**

The ability to manipulate individual atoms by means of scanning tunneling microscopy (STM) opens op opportunities for storage of digital data on the atomic scale. Recent achievements in this direction include data storage based on bits encoded in the charge state, the magnetic state, or the local presence of single atoms or atomic assemblies. However, a key challenge at this stage is the extension of such technologies into large-scale rewritable bit arrays. We demonstrate a digital atomic scale memory of up to 1 kilobyte (8,000 bits) using an array of individual surface vacancies in a chlorine terminated Cu(100) surface. The chlorine vacancies are found to be stable at temperatures up to 77 K. The memory, crafted using scanning tunneling microscopy at low temperature, can be read and re-written automatically by means of atomic scale markers, and offers an areal density of 502 Terabits per square inch, outperforming state-of-the-art hard disk drives by three orders of magnitude.

5:40pm **AM+MP+NS-WeA11 Extending the Capabilities of STM-based Dopant Device Fabrication***, T. Skeren, N. Pascher, S.A. Köster, **Andreas Fuhrer**,* IBM Research - Zurich, Switzerland **INVITED**

Since the invention of the first bipolar transistor, integrated circuits have evolved to incredibly complex, ultra-scaled devices with on the order of 10^9 transistors per chip. Even if these devices no longer rely on bipolar technology, excellent control of highly doped regions is still a critical factor for device performance. Moreover, single dopant atoms in a silicon crystal or nanoscale silicon transistors are thought to be candidates for spin qubits with a long spin lifetime.

The hydrogen resist lithography technique is capable of preparing atomic scale planar dopant devices. This is enabled by a large difference in chemical reactivity of the bare and hydrogen passivated Si (001): 2x1 surface. Using a scanning tunneling microscope (STM), the hydrogen layer of the H:Si (001) surface is locally desorbed with nanometer precision, exposing areas of reactive Si. When a gaseous dopant precursor such as phosphine or diborane is introduced, the hydrogen layer acts as a resist and the dopants stick only to the desorbed areas. Compared to conventional fabrication methods, hydrogen resist lithography enables degenerate d-doping with sub-nanometer lateral resolution and abrupt doping profiles.

We have extended the hydrogen-resist technique to p-type doping with diborane and present electrical transport measurements on p-type dopant wires and a simple planar pn-junction fabricated by STM patterning.

In addition, we have developed a CMOS compatible device platform for STM-based atomic-scale device fabrication. The scheme uses pre-fabricated samples with electrical contacts and alignment markers and a hydrogen terminated, reconstructed Si:H(001) surface that is protected from the ambient environment by a capping chip.

The sample surface can be used directly for STM-patterning and atomic device fabrication after in-situ removal of this capping chip. After STM device-fabrication the samples are reintegrated into the CMOS workflow by hydrophobic bonding for wafer scale contacting.

Full functionality of this approach is demonstrated with magnetotransport measurements on degenerately doped STM patterned Si:P nanowires up to room temperature, made possible by the use of silicon on insulator substrates.

Applied Surface Science Division
Room 204 - Session AS+SE-WeA

Industrial and Practical Applications of Surface Analysis

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

2:20pm **AS+SE-WeA1 Identification of Unknown Contaminants in Industrial Applications Using MS/MS in Combination with High Resolution Mass Spectrometry***, A. Pirkl, **Julia Zakel**, D. Rading,* IONTOF GmbH, Germany*; N.J. Havercroft,* IONTOF USA*; S. Kayser, H. Arlinghaus, R. Moellers, E. Niehuis,* IONTOF GmbH, Germany

The fast and reliable characterisation of unknown contaminants in quality control procedures is crucial in many industrial areas to understand manufacturing errors and avoid production downtime. TOF-SIMS nowadays plays an important role in this area especially due to its fast imaging capabilities that enable the acquisition of chemical surface images with a lateral resolution in the 100 nm range.

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

Different applications ranging from polymers to metals will be presented with a focus on the identification of unknown substances by MS/MS in combination with high resolution mass spectrometry. Furthermore dedicated measurement modes and strategies that can be applied to different forms of contaminants will be presented. The use of databases will be showcased which further assists and confirms the results of a manual data evaluation.

[1] The 3D OrbiSIMS – Label-Free Metabolic Imaging with Sub-cellular Lateral Resolution and High Mass Resolving Power, Passarelli et al., Nature Methods, 2017, 14(12):1175-1183, DOI 10.1038/nmeth.4504.

2:40pm **AS+SE-WeA2 ToF-SIMS Analysis of Glass and Glass Coatings**, ***Christine Mahoney***, Corning Inc.

Many think of glass as being an inert material. However, glass contains many reactive alkalis and other elements that can interact and diffuse into solutions or into coatings. These alkalis tend to decrease the chemical durability of the glass itself, and can play a key role in accelerating corrosion and delamination mechanisms involving the glass. How we manufacture and process the glass plays a significant role in its chemical durability and reactivity. The reactivity of a glass surface can be particularly problematic for pharmaceutical applications, where glass delamination in vials and/or drug interactions with glass constituents can potentially occur. Here we present an overview of ToF-SIMS research at Corning involving the analysis of glass surfaces and their associated coatings. Both organic and inorganic applications will be discussed, using a wide range of tools for analysis.

3:00pm **AS+SE-WeA3 Problem Solving with Valence Band Spectroscopy and SIMS MS/MS**, ***Steven Pachuta***, *D.M. Poirier,* 3M Company **INVITED**

Surface chemistry is often key to the performance of materials like films, coatings, and adhesives. Controlling and understanding surface chemistry is therefore critical to manufacturers. X-ray photoelectron spectroscopy (XPS) is the workhorse in industrial surface characterization laboratories, followed closely by time-of-flight secondary ion mass spectrometry (ToF-SIMS). XPS survey spectra provide quantitative elemental information on surfaces, and XPS high energy-resolution spectra can give information on chemical states. ToF-SIMS, in general, gives even more specific surface chemical information, such as the identities of polymer additives and surface contaminants.

This presentation will describe efforts to increase the chemical specificity of both XPS and ToF-SIMS for organic species, especially polymers. The XPS valence band region contains a complex fingerprint which is highly dependent on molecular structure. By using databases in combination with multivariate methods such as principal component analysis (PCA) and partial least squares (PLS), a surprising degree of information can be extracted from valence band spectra of unknown materials.

The fact that many real-world surfaces comprise a mixture of components is a recurrent frustration in industrial surface characterization. ToF-SIMS analysts have long envied their GC/MS and LC/MS counterparts, who have the luxury of separating mixtures before doing mass spectrometry. The recent commercial availability of tandem mass spectrometry (MS/MS) on ToF-SIMS instruments has gone some way towards addressing the mixture problem and has increased the ability of ToF-SIMS to identify unknown materials. Examples will be presented.

4:20pm **AS+SE-WeA7 *Surface and In-depth XPS Characterization of Liquid and Cured Control Release Additives (CRAs) Used in Silicone-Based Release Coatings***, ***Brian Strohmeier***, *K. Rhodes, R. Munigeti, J. Orlowski,* Avery Dennison Corporation

Silicone-based release coatings are used in a wide variety of commercial applications including: release liners for removable pressure sensitive adhesive laminates and tapes, release papers and polymer films, non-stick packaging, and other products where a specific force of peel separation is required between two different film materials during processing or storage. Typical industrial silicone-based release coatings consist of UV or heat cured mixtures of silicone compounds and controlled release additives (CRAs). CRAs commonly contain proprietary mixtures of functionalized silanes, siloxanes, and silica, plus a variety of other organic components. The release properties of silicone-based release coatings depend highly on the distinct types and relative amounts of the silicone compounds and CRAs used in the cured mixture. Therefore, it is of great interest to quantitatively characterize the silicone and CRA components on the surface of silicone release coatings for improved product and process development as well as problem-solving related to release issues. In this study, a variety of commercial CRA products were characterized by gel permeation chromatography (GPC) for bulk molecular weight distribution information and by X-ray photoelectron spectroscopy (XPS) for surface composition and chemistry. The CRA materials studied had vapor pressures that allowed successful XPS characterization in the liquid state. Surprisingly, the CRA liquids could even be sputtered and/or depth profiled using argon cluster ions, whereas sputtering with monatomic argon ions resulted in XPS chemical state changes caused by ion beam induced sample damage. The CRA materials were characterized by XPS and argon cluster ion sputtering/depth profiling in the pure liquid state and in solid heat cured release coating mixtures with polydimethyl siloxane (PDMS). The high resolution Si 2p XPS spectra obtained for cured silicone release coatings of known composition could be peak-fitted into separate CRA and PDMS components to produce a quantitative calibration curve for evaluating release coatings with unknown CRA/silicone compositions.

4:40pm **AS+SE-WeA8 Differentiating Silicones Using SIMS**, ***Paul Vlasak***, *M.L. Pacholski,* The Dow Chemical Company

The unique properties of poly(dimethylsiloxane), also known as PDMS or silicone, have allowed PDMS-based materials to proliferate in modern industry. A huge variety of applications using PDMS have been developed including structural adhesives, release agents, optical components, lubricants, anti-foam agents, and potting agents to name a few. Considering the omnipresence of PDMS in industrial settings along with its low surface energy and tendency to migrate, it comes as no surprise that PDMS is frequently encountered in industrial surface analysis laboratories. Because PDMS is readily detected and easily recognized by its characteristic fragmentation pattern, SIMS is well suited to identifying the presence of silicones on a wide range of materials.

In some instances, the analyst expects to find PDMS on a sample surface. For example, the PDMS transferred from a silicone release liner onto an adhesive may be of interest. In other instances, PDMS can be encountered as an unexpected contaminant, perhaps interfering with adhesion or causing defects in a coating or painting operation. In either case, besides its mere presence, the structural details of the PDMS may be important to understanding the behavior of the adhesive/release system or discovering the actual source of a contaminant amongst multiple possibilities.

From a pragmatic standpoint, the current work explores how molecular weight, endgroup type, and other structural factors influence PDMS fragmentation patterns through the use of well-characterized reference materials. The effects of instrument-related parameters as well as film thickness and substrate type will also be considered to the extent these factors influence the spectra obtained.

5:00pm **AS+SE-WeA9 Uranium Particles Analysis and Imaging Using ToF-SIMS for Source Identification**, ***Juan Yao***, *E. Krogstad, S. Shen, Z.H. Zhu, X-Y. Yu,* Pacific Northwest National Laboratory

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a highly surface sensitive analytical tool. It offers excellent limits of detection (LODs) of part per million with sub-micron spatial resolution. Besides determining isotopic ratios of radioactive materials, ToF-SIMS has the advantage of providing full mass spectra with m/z up to 2000 Da, allowing the detection of chemical signatures in a material. This latter feature is very attractive to identify the source of uranium and other radioactive materials in single particles. We analyzed three different NIST standard reference materials with varied concentrations of uranium in this study. Samples are in the form of glass wafers and particles deposited on a substrate. By applying spectral principal component analysis (PCA), the SIMS mass spectra obtained from the same type of NIST sample show consistent features; regardless of the sample form. Furthermore, a blind test was conducted using a mixture consisting of particles from all three NIST materials. Our spectral PCA results illustrate that ToF-SIMS can be a useful tool to differentiate particles of different origins and potentially applicable for signature identification in single particles. In addition, scanning electron microscopy (SEM) was applied to complement the SIMS imaging for correlative analysis [1]. It is beneficial to use SEM to obtain particle morphological information. However, SEM lacks the sensitivity in single particle elemental analysis compared to ToF-SIMS. Our work demonstrates that ToF-SIMS is a powerful tool for analysis of individual radioactive particles to fulfill nuclear safeguards and forensic missions.

5:40pm **AS+SE-WeA11 Application of X-ray Photoelectron Spectroscopy to Degradation Studies of Electrodes in Fuel Cells and Electrolyzers**, ***Kateryna Artyushkova***, University of New Mexico; *N. Danilovic,* Lawrence Berkeley Lab, University of California, Berkeley; *C. Capuano,* Proton on site; *A. Serov,* Pajarito Powder LLC; *P. Atanassov,* University of New Mexico

The stability of materials used used in anodes and cathodes in fuel cells and electrolyzers is a critical factor for practical industrial applications. To improve the longevity, it is important to link the chemical structure to degradation mechanisms and changes in the surface composition of the catalyst on the electrodes. Application of x-ray photoelectron spectroscopy (XPS) to probe structure of catalytic materials and their degradation is becoming an important analytical approach due to its accessibility and quantitative chemical information provided. This talk will present several examples of application of high-resolution XPS for analysis of the chemistry of electrodes and changes that are occurring during operation in several technological platforms, such as proton-exchange membrane fuel cells (PEMFCs), alkaline membrane fuel cells (AEMFC), direct methanol fuel cells (DMFC), direct hydrazine fuel cells (DHFC) and water electrolyzers (WE).

Biomaterial Interfaces Division
Room 104B - Session BI+AC+AS+HC+NS+SS+TF-WeA

Current and Future Stars of the AVS Symposium II

Moderator: David Boris, U.S. Naval Research Laboratory

2:20pm **BI+AC+AS+HC+NS+SS+TF-WeA1 Medard W. Welch Award Lecture: A Surface Scientist's Journey from Small Molecules to Biomolecules and Biomaterials***, David G. Castner*[1]*,* University of Washington **INVITED**

Surface science plays an important role in a wide range of research and development areas such catalysis, biomaterials, microelectronics, clean energy and corrosion. The toolbox of surface scientist allows us to easily move across research topics and make significant impacts in both industrial and academic settings. The typical surface scientist is an expert in multiple techniques, surface modification, sample preparation/handling and instrumentation. We have all benefited from the significant and numerous advances that have occurred in the past 40 years in terms of improved instrumentation, introduction of new techniques and development of sophisticated data analysis methods, which has allowed us to perform detailed analysis of increasing complex samples. For example, comprehensive analysis of surfaces and surface immobilized molecules with modern surface science instrumentation provides an unprecedented level of detail about the immobilization process and the structure of the immobilized molecules. Results from x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), near edge x-ray absorption fine structure (NEXAFS), surface plasmon resonance (SPR) and quartz-crystal microbalance with dissipation (QCM-D) biosensing, atomic force microscopy, and sum frequency generation (SFG) vibrational spectroscopy combined with computation methods such as molecular dynamic (MD) and Monte Carlo (MC) simulations provide important information about surface chemistry and structure. However, even with the advances that have been achieved with these powerful surface science techniques, there still remain many significant challenges for surface scientist. These include characterizing the surface chemistry and structure of nanoparticles, determining the atomic level structure of complex molecules bound to surfaces, 3D imaging of samples, and improved sample preparation methods that maintain materials in a relevant state when using ultra-high vacuum based analysis techniques.

This talk will discuss my adventures as a surface scientist starting from chemisorption and reactivity studies of small molecules on single crystal surfaces followed by industrial catalysis research and eventually moving to biomedical surface analysis with side ventures into areas such as clean energy. It has been an exciting journey and I will use it to provide some examples of the multidisciplinary nature of surface science as well as discuss opportunities for addressing future challenges.

3:00pm **BI+AC+AS+HC+NS+SS+TF-WeA3 Invited Talk-Future Stars of AVS Session: Making, Studying, and Designing Hierarchically Structured Soft Materials***, Keith A. Brown*[2]*,* Boston University

Nature realizes extraordinary materials by structuring them precisely from the molecular scale to the macroscopic scale. While nature may have perfected this process over evolutionary time scales, synthetically recapitulating this level of control is tremendously difficult due to the large number of length scales involved and our limited knowledge of interactions between these scales. Faced with the daunting challenge of synthetically realizing soft hierarchical materials, we have adopted a three pronged strategy to: (1) make structures with control from the molecular scale to the macroscopic scale by directing bottom-up growth processes with top-down control, (2) learn how the properties of such materials emerge from their hierarchical structure, and (3) design the best performing structures using novel approaches borrowed from machine learning and autonomous research. In this talk, we will on report recent progress in this complementary areas of making, studying, and designing hierarchical materials. In particular, we will focus on two major classes of materials, nanoparticle-based structures where the assembly and organization of particles leads to emergent mechanical properties at the bulk scale and polymer-based materials where we are connecting the synthesis, patterning, and properties of polymer structures across scales. In addition to lessons about the fundamental properties of hierarchically organized soft matter, we will highlight the synergies possible when combining, synthesis, detailed characterization, and advances in materials design.

3:20pm **BI+AC+AS+HC+NS+SS+TF-WeA4 Invited Talk-Future Stars of AVS Session: Vapor Phase Infiltration for Transforming Polymers into Hybrid Materials: Processing Kinetics and Applications***, Mark Losego*[3]*,* Georgia Institute of Technology

Vapor phase infiltration (VPI) is an emerging processing technology for infusing polymers with inorganic constituents to create new organic-inorganic hybrid materials with novel chemical, electrical, optical, and/or physical properties. These new hybrid materials have demonstrated applications including chemical separations, photovoltaics, and microelectronics patterning. This talk will focus on our development of a fundamental VPI processing kinetics phenomenology to create a pathway for rational design of material composition and structure. By measuring VPI compositional profiles as a function of space or time and temperature, we can extract fundamental energy barriers for the sorption, diffusion, and reaction processes and delineate amongst different rate limiting steps. In our materials development, we often find that partial infiltration of a polymer film, fiber, or foam is sufficient to impart desired properties; so rational design of the infiltration kinetics can enable desired performance without waste in processing time or materials. Here, we will demonstrate several examples including our work to create chemically insoluble polymers and membranes. We find, for example, that infiltration depths of about 0.75 microns are sufficient to yield PMMA chemically insoluble in organic solvents regardless of whether it is in a thin film geometry or a macroscopic plexiglass object of centimeters in dimension. In PIM-1 membranes used for chemical separations, we find that we can achieve > 30 wt% inorganic loading with a single infiltration exposure. After infiltration, these membranes become stable in new separations solvents that previously swelled and/or dissolved the polymer.

(Submitted for the Future Stars of the AVS Symposium.)

4:20pm **BI+AC+AS+HC+NS+SS+TF-WeA7 Invited Talk-Future Stars of AVS Session: Surface Preparation Methods for the Selective Oxidation of Ethanol to Acetaldehyde over TiO_2/Au(111)***, Ashleigh Baber*[4]*, D.T. Boyle, J. Wilke, V. Lam, D. Schlosser,* James Madison University

Obtaining a molecular-level understanding of the reaction of alcohols with heterogeneous model catalysts is critical for improving industrial catalytic processes, such as the production of hydrogen from alcohols. The use of reducible oxides provides a source of oxygen on Au(111) for the reaction of ethanol, which is easily regenerated in the presence of an oxygen background. 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. Depending on the surface preparation conditions, Au(111) supported TiO_2 nanoparticles react with small alcohols to form either reduced and oxidized products. The desire to selectivity form oxidized or reduced products merits an investigation of alcohol reactivity over differently prepared TiO_2/Au(111) surfaces. In this work, a systematic study of ethanol reactivity over several TiO_2/Au(111) surfaces elucidates the effect of surface conditions on the selectivity of the reaction between ethanol and TiO_2/Au(111). The reactivity of the surface for ethanol oxidation was altered by controlling the oxidation state of TiO_x (x<2). Atomic force microscopy (AFM) provides information regarding the structure of the Au(111) supported TiO_2 nanoparticles and ultrahigh vacuum temperature programmed desorption (TPD) monitors the selectivity of the reaction between ethanol and TiO_2/Au(111). 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. Low coverages of fully oxidized TiO_2 nanoparticles on Au(111) are active for the selective oxidation of ethanol to form acetaldehyde.

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

[2] **Future Stars of the AVS**

[3] **Future Stars of the AVS**

[4] **Future Stars of the AVS**

4:40pm **BI+AC+AS+HC+NS+SS+TF-WeA8 Invited Talk-Future Stars of AVS Session: Single Atom Catalysis: An Atomic-Scale View*, Gareth Parkinson*[1]*,*** TU Wien, Austria

Single-atom catalysis is a rapidly emerging area of research that aims to maximize the efficient usage of precious metals through ”single atom” active sites. Although catalytic activity has been demonstrated for several single-atom catalyst systems, an inability to accurately characterize the catalyst based on single atom active sites ensures that that the field remains controversial, and little is really known about how a single atom adsorbed on a metal oxide support catalyzes a chemical reaction. In this lecture, I will describe how we are addressing the crucial issues of stability and reaction mechanism using a surface science approach. The work is based on the magnetite (001) surface, which exhibits an unusual reconstruction based on subsurface cation vacancies.

The surface stabilizes ordered arrays of metal adatoms (of almost any variety) with a nearest neighbor distance of 0.84 nm to unprecedented temperatures as high as 700 K. Crucially, because the geometry of the adatoms is uniform and precisely known, reactivity experiments are performed on a well-defined model system, and theoretical calculations can be performed to shed light on the mechanisms at work. Several examples of our recent work will be used to illustrate the trends discovered to date, including how strong CO adsorption destabilizes Pd and Pt adatoms leading to rapid sintering, and how extraction of lattice oxygen from the metal-oxide is central to catalytic activity in the CO oxidation reaction.

5:00pm **BI+AC+AS+HC+NS+SS+TF-WeA9 Invited Talk-Future Stars of AVS Session: Multimodal Chemical and Functional Imaging of Nanoscale Transformations Away from Equilibrium*, Olga Ovchinnikova*[2]*,*** Oak Ridge National Laboratory

The key to advancing energy materials is to understand and control the structure and chemistry at interfaces. While much of the dynamic chemistry can be studied on macro-scale systems, there is a lack of means to localize chemical measurements and correlate them to nanoscale structure of the material. Through a unique merger of advanced scanning probe microscopy and mass spectrometry techniques rooted in innovative data processing and control algorithms, we are now able to understand the interplay between chemical and physical functionality at the fundamental length using multimodal chemical imaging. This multimodal imaging transcends existing techniques by providing nanoscale structural imaging with simultaneous quantitative nanomechanical properties and quantitative chemical analysis. In this talk I will discuss how we have developed and used this capability to visualize dynamic material transformations at interfaces, to correlate these changes with chemical composition, and to distil key performance-centric material parameters. One exciting capability is that the AFM can be used to drive materials away from equilibrium at the nanoscale with highly localized electric fields. This allows field confinement effects on localized chemistry in materials to be locally probed, especially at interfaces. This in turn yields direct information on key energy related questions such as electron and ion motion distribution and transport at and between interfaces. We have applied this approach to the study of systems and processes that underlie energy capture, conversion and storage, including photovoltaics and oxide ferroelectrics, which have historically eluded comprehensive understanding of the mechanisms behind the spatially heterogeneous interfacial chemistry and its link to material performance. Overall, I will focus on ways to unlock the mystery of active interface formation through intertwining data analytics, nanoscale elemental and molecular characterization, with imaging; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

5:20pm **BI+AC+AS+HC+NS+SS+TF-WeA10 Invited Talk-Future Stars of AVS Session: Expanding the Structural Toolkit to Characterize Heavy Actinide Complexes*, Rebecca Abergel*[3]*,*** Lawrence Berkeley Lab, University of California, Berkeley*; G. Deblonde, A. Mueller, P. Ercius,* Lawrence Berkeley National Laboratory*; A.M. Minor,* Lawrence Berkeley Lab, University of California, Berkeley*; C.H. Booth, W.A. de Jong,* Lawrence Berkeley National Laboratory*; R. Strong,* Fred Hutchinson Cancer Research Center

Structural characterization of actinide elements from actinium to einsteinium can be a challenging task due to the high radioactivity and limited availability of some of the isotopes of interest. However, significant work is needed to address a certain lack of understanding of the fundamental bonding interactions between those metal centers and selective ligands. Such understanding presents a rich set of scientific challenges and is critical to a number of applied problems including the development of new separation strategies for the nuclear fuel cycle, the need for decontamination after a nuclear accident or the use of radio-isotopes for new cancer treatments. Our studies utilize luminescence sensitization, UV-Visible, X-ray absorption, and X-ray diffraction spectroscopic techniques as well as transmission electron microscopy and electron energy loss spectroscopy to investigate specific heavy actinide coordination features. Using simple inorganic complexes but also strong hard oxygen-donor ligands as well as more elaborate higher molecular weight protein assemblies allows the differentiation of heavy actinide species even when limited to minute amounts of materials. Innovative structural characterization approaches based on X-ray absorption, X-ray diffraction and electron microscopy that were applied to series of isostructural systems and used to derive coordination trends in the later 5*f*-element sequence will be discussed.

5:40pm **BI+AC+AS+HC+NS+SS+TF-WeA11 Invited Talk-Future Stars of AVS Session: Trends in Adsorbate Interactions with Bimetal Surfaces*, Liney Arnadottir*[4]*,*** *L.H. Sprowl,* Oregon State University

Surface chemistry plays an important role in a large range of applications and technologies, such as catalysis and electrocatalysis, device fabrication through film growth, and degradations through oxide formation, carbonization, and corrosion. Bimetal surfaces are of increasing interest for single atom catalysis and corrosion resistance of alloys. Previous studies have shown correlations between adsorbate interactions and d-band shifts for different metals as well as for alloying effects of metal sandwich structures, but for mixed metal surfaces the nature of the adsorption site can change (ensemble effect) as well as the number of electrons in the surface layer which effects the d-band center. Here we explore correlations of adsorbate interactions with mixed metal surfaces through density functional theory calculations of adsorbate interactions with different facets, (100) and (111), of pure Ni and eleven Ni-based surface alloys as well as Ni in different host metal. We find that the addition of surface alloying atom has little effect on the binding of CO and C but C binding varies for different facets. On the other hand, O binding is highly dependent on the alloying element due to ensemble effect. This has an interesting effect on the predicted reaction energies of CO dissociation which is endothermic on the (111) facet and exothermic on the (100) facet governed by C interactions but the changes in the reaction energy within each facet are mostly governed by the ensemble effect on O adsorption. The relationship between the formation energy of the mixed metal surface and adsorbate interactions will also be discussed.

Biomaterial Interfaces Division
Room 101B - Session BI-WeA

Microbes and Fouling at Surfaces

Moderator: Caitlin Howell, University of Maine

3:00pm **BI-WeA3 Gaede-Langmuir Award Lecture: From Description to Prediction of Biointerphase Reactions*, Michael Grunze*[5]*,*** Max Planck Institute for Medical Research, Germany*; H.J. Kreuzer,* Dalhousie University, Canada **INVITED**

Many experiments in Biointerphase Research aim to determine the number of cells or organisms adsorbing on a surface. In order to discriminate between physisorbed and settled cells, a rinsing step is applied when the sample is removed from solution. However, no information is obtained which shear flow is required to overcome the activation barrier of detachment to remove the cell. In this lecture I want to address the question to what extend we can use the formalism derived in gas phase adsorption and desorption experiments to describe the analog reactions in solution quantitatively and predictably? Predictive models would help to advance microfluidic based diagnostics and contribute to the design of environmental benign anti-fouling surfaces.

Recent experiments and theoretical work to understand adsorption and detachment of small (cell size) objects from a surface under shear flow will be discussed with reference to the formalism used in basic gas phase adsorption/desorption experiments. In the most basic experiments, the

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[1] **Future Stars of the AVS**

[2] **Future Stars of the AVS**

[3] **Future Stars of the AVS**

[4] **Future Stars of the AVS**

[5] **Gaede Langmuir Award Winner**

probability that a molecule will adsorb or desorb is measured as a function of pressure, temperature, and coverage. Monolayer adsorption of a gas is described by the Langmuir isotherm (or its derivatives if interactions between the molecules need to be considered) and desorption by an Arrhenius type equation to determine the activation energies.

The kinetic equation used in gas phase experiments can be modified to describe adsorption and detachment of particles from a surface under shear flow, where temperature is replaced by shear force to determine activation energies. The shear force is ramped up in a programmable way, and by fitting the experimental data with a rate equation gives highly reproduceable results from which the activation energy of detachment of these particles can be derived. The activation energy values determined from these experiments will be discussed in the context of separately measured adhesion energies of these particles in an aqueous environment to derive a mechanistic understanding for attachment and detachment of small objects in laminar shear flow.

4:20pm **BI-WeA7 Unraveling Complexities at the Adhesive Interface of Acorn Barnacles**, ***Kenan Fears****, C.R. So, D.H. Leary, H. Ryou, J. Schultzhaus, C. Wang,* US Naval Research Laboratory*; B. Orihuela, D. Rittschof,* Duke University Marine Laboratory*; C.M. Spillmann, K.J. Wahl,* US Naval Research Laboratory **INVITED**

Marine macro-foulers (e.g, barnacles, tubeworms, mussels) create robust underwater adhesives capable of attaching themselves to almost any material. While proteomic analysis has provided insight into the chemical composition of these natural adhesives, developing synthetic analogs that mimic their performance remains a challenge due to an incomplete understanding of adhesion processes. Through the use of in vivo confocal microscopy with multiple fluorescent probes, we have identified that acorn barnacles (*Amphibalanus (= Balanus) amphitrite*) secrete a phase-separating surfactant mixture to clean and protect the surface ahead of growth and cement deposition. This mixture consists of a phenolic laden gelatinous phase that holds a phase rich in lipids and reactive oxygen species at the seawater interface. This secretion oxidizes and lifts off adhered biofilms surrounding the barnacle base as it expands. These findings show barnacles repurpose phenolic chemistries ubiquitious to adhesives and cuticles as part of their own antifouling strategy. The discovery of this critical step in underwater adhesion represents a missing link between natural and synthetic adhesives, and provides new directions for the development of environmentally-friendly biofouling solutions.

5:00pm **BI-WeA9 Ultra Low Fouling Zwitterionic Coatings – Influence of Molecular Architecture on Fouling Inhibition**, ***Axel Rosenhahn****, J. Koc,* Ruhr-University Bochum, Germany*; S. Bauer,* Ruhr-Universität Bochum, Germany*; J. Finlay, A.S. Clare,* Newcastle University*; E. Schoenemann,* University of Potsdam*; A. Laschewsky,* University of Potsdam

Zwitterionic polymers are promising ultra-low fouling coating materials. While their outstanding properties are undisputed, a precise understanding of how the molecular architecture leads to optimized polymer function is still missing. Here we compare the influence of different anionic groups using a range of self-assembled monolayers and compare it against a series of photocrosslinkeable zwitterionic polymers. In all cases, the intramolecular arrangement was varied in order to determine if the spacing between the oppositely charged moieties, the nature of the charged group, and the backbone affect their non-fouling properties. A comparison of self-assembled monolayers consisting of mixed, oppositely charged thiols and custom designed zwitterioinic thiol compounds showed that in particular sulfate groups showed promising properties and an horizontally adjacent arrangement was preferred. As approach towards polymeric coatings, zwitterionic methacrylates were co-polymerized with benzophenonemethacrylates to obtain a photocrosslinkable polymer. We applied the polymers by spin-coating and subsequent photocrosslinking. All coatings were characterized by AFM, IR, and XPS prior to biological testing and protein resistance was characterized by SPR. The antifouling activity against marine biofilm formers, algae, and invertebrate larvae was determined in laboratory assays. On the basis of the obtained data, design criteria for optimized zwitterionic components for fouling-release technologies will be discussed.

5:20pm **BI-WeA10 Biomimetic Surfaces on Chitosan Membranes with Enhanced Antibacterial Properties Produced by Directed Plasma Nanosynthesis**, ***Camilo Jaramillo****, A.F. Civantos, J.P. Allain,* University of Illinois at Urbana-Champaign

First reported in the late 1950s, antibiotic-resistant bacteria have become an issue of major concern [1]. This has motivated the study of other mechanisms to provide interfaces with antibacterial activity, including surface chemistry, surface topography and other physicochemical properties [2]. Among these mechanisms, the physico-mechanical effects have also attracted attention. An example of this concept can be found in natural nanostructured surfaces. The nanopatterned surface of the cicada wings has been observed to possess very effective bactericidal activity, via a chemistry-independent mechanism [3]. Chitosan, a biodegradable and non-toxic biopolymer with antibacterial properties, has been used for wound treatment, drug delivery and biosensing applications [4]. These properties make it an attractive material to be used in biointerfaces. Following the same concept of the cicada wings, nanopatterned silicon surfaces coated with CS showed enhanced antibacterial activity, when compared to un-coated Si surfaces [5].

In previous works from our group, we had shown that Directed Plasma Nanosynthesis (DPNS) can induce the formation of nanofeatures on the surface of chitosan. In this work, we further study the effects of DPNS on the formation of nanopatterns on the surface of different chitosan membranes are further studied, using angle of irradiation as a control parameter. Additionally, the biocidal action of the modified surfaces is studied by running in vitro tests with *E. coli*. SEM images were used to evaluate the nanofeatures induced on the surfaces, as well as their effects on the incubated bacteria. Studying the antibacterial activity of these nanopatterned surfaces constitutes a step towards elucidating the mechanisms of antibacterial activity based on physico-mechanical effects.

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5:40pm **BI-WeA11 How Do Geobacter Aggregates Communicate: New Understanding from In Situ Liquid SIMS**, ***Wenchao Wei****, R. Komorek,* Pacific Northwest National Laboratory*; C. Yang, F. Liu,* Yantai Institute of Coastal Zone Research*; Z.H. Zhu, X-Y. Yu,* Pacific Northwest National Laboratory

We developed a vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI), to enable direct observations of liquid surfaces and liquid-solid interactions using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and a variety of spectroscopy and microscopy characterization techniques. SALVI was recently applied to investigate biological interfaces in living biofilms and co-cultured microbial communities [1, 2]. In this talk, a more complex microbial communities consisting of syntrophic *Geobacter metallireducens* and *Geobacter sulfurreducens* was investigated using ToF-SIMS [3]. As a surface technique, in situ liquid SIMS provides direct measurement of initial attachment of the co-cultured aggregates. Our 3D imaging results give spatial distribution of amino acid fragments and lipids, indicative of the role of proteins and lipids played in the co-cultured aggregate formation. The planktonic cells seem to show strong evidence of hydrogen transfer in liquid by the direct observations of lipid fragments with the addition of water and hydrogen. This pheromone indicates that higher direct electron interspecies transfer may exist in co-culture aggregates whereas hydrogen transfer is dominant in planktonic cells. More interestingly, distinct water distribution is observed between co-cultured aggregates and planktonic cells, indicating the change of hydrogen bonding as a result of the complex microbial syntrophic community communication. Our results demonstrate that interfacial chemistry involving living microbial systems can be studied from the bottom up based on microfluidics, potentially providing more important understanding in system biology.

Key words: microfluidics, biofilm, co-cultured aggregate, electron transfer, EPS, ToF-SIMS

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Electronic Materials and Photonics Division
Room 101A - Session EM+2D+SS-WeA

Wide and Ultra-Wide Bandgap Materials for Electronic Devices: Growth, Modeling and Properties

Moderators: Erica Douglas, Sandia National Laboratories, Rachael Myers-Ward, U.S. Naval Research Laboratory

2:40pm **EM+2D+SS-WeA2 2300 V Reverse Breakdown Voltage Ga_2O_3 Schottky Rectifiers***, **Jiancheng Yang**[1], F.R. Ren,* University of Florida*; M.J. Tadjer,* U.S. Naval Research Laboratory*; S.J. Pearton,* University of Florida*; A. Kuramata,* Tamura Corporation and Novel Crystal Technology, Inc., Japan

A reverse breakdown voltage of 2300 V with corresponding breakdown field of 1.15 MV/cm was demonstrated for 20 µm epi-β-Ga_2O_3 edge-terminated vertical Schottky rectifiers. This breakdown voltage is the highest ever reported for Ga_2O_3 rectifiers. Ga_2O_3 has an energy band gap of range 4.5 – 4.9 eV, which correlates to the theoretical breakdown electric field of ~8 MV/cm. The theoretical Baliga figure of merit (defined as V_B^2/R_{ON}, where V_B is the reverse breakdown voltage and R_{ON} is the on-state resistance) of Ga_2O_3 estimated to be 400% higher than GaN.[1] Previously reported, an unterminated Ga_2O_3 rectifier shown a breakdown voltage of 1600 V, and a field-plated Schottky diode has a breakdown voltage of 1076 V with the epi thickness 7 µm [2,3] This work has shown the improvement of the Ga_2O_3 vertical rectifiers breakdown voltage using a field-plate terminated approach with a lightly doped 20 µm Ga_2O_3 epitaxial layer . The edge-terminated Schottky rectifiers of various dimensions (circular geometry with diameter of 50-200 µm and square diodes with areas 4×10^{-3}- 10^{-2} cm^2) fabricated on 20µm lightly doped ($n=2.10 \times 10^{15}$ cm^{-3}) β-Ga_2O_3 epitaxial layers grown by hydride vapor phase epitaxy on conducting ($n=3.6 \times 10^{18}$ cm^{-3}) Ga_2O_3 substrates grown by edge-defined, film-fed growth. The R_{ON} for these devices was 0.25 Ω-cm^2, leading to a figure of merit (V_B^2/R_{ON}) of 21.2 MW/cm^2. The Schottky barrier height with the Ni/Au based metallization was 1.03 eV, with an ideality factor of 1.1 at room temperature. The Richardson's constant of 43.35 A/cm-K^2 was extracted from the temperature dependent forward IV. The breakdown voltages for the different size devices ranged from 1400-2300V, with a general, but not a linear trend of decreasing breakdown voltage for larger area rectifiers. The diode reverse recovery time of ~22 ns was measured by switching the diode from +2V to -2V.

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3:00pm **EM+2D+SS-WeA3 Characterization of β-$(Al,Ga,In)_2O_3$ Epitaxial Films for UV Photodetector Applications***, **Luke Lyle**, L.M. Porter, R. Davis,* Carnegie Mellon University*; S. Okur, G.S. Tompa,* Structured Materials Industries, Inc.*; M. Chandrashekhar, V. Chava, J. Letton,* University of South Carolina

β-Ga_2O_3 has garnered increased attention over the last few years due to its ultra-wide bandgap of ~5.0 eV and the ability to grow Ga_2O_3 single crystals from the melt. In addition to its desirability for high power electronics, Ga_2O_3 is well suited for solar-blind UV photodetectors. These detectors are coveted by numerous industries and the military for applications ranging from flame- and missile-plume detection to ozone hole monitoring. In this study we have grown $(Al,Ga,In)_2O_3$-based alloy epitaxial films on sapphire via metalorganic chemical vapor deposition (MOCVD) to investigate their potential application for wavelength-tunable UV photodetectors. The films were characterized structurally, optically, and chemically using x-ray diffraction (XRD), optical transmittance, and energy dispersive x-ray spectroscopy (EDX). Based on XRD and EDX results, β-$(Al_xGa_{1-x})_2O_3$, β-$(In_xGa_{1-x})_2O_3$, and β-Ga_2O_3 epitaxial films with compositions through x = 0.29 (for Al) and x = 0.13 (for In) were grown. The optical bandgap was found to correspondingly vary between 5.5±0.1 and 4.3±0.3 eV, as a function of composition. MSM- and Schottky-based solar-blind UV photodetectors were also fabricated on selected films. The devices showed responsivities up to 1E5 A/W and quantum efficiencies up to 6E5 at 220 nm from a deuterium lamp. The wavelength tunability of the photodetectors is currently being investigated and will be discussed in this presentation.

3:20pm **EM+2D+SS-WeA4 High Three-terminal Breakdown Voltage Quasi-two-dimensional β -Ga_2O_3 Field-effect Transistors with a Dual Field Plate Structure***, **Jinho Bae**,* Korea University, Republic of Korea*; H.W. Kim, I.H. Kang,* Korea Electrotechnology Research Institute (KERI), Republic of Korea*; G.S. Yang, S.Y. Oh, J.H. Kim,* Korea University, Republic of Korea

β-Ga_2O_3 is an intriguing material because of its large direct bandgap (4.85 eV), high breakdown field (~8 MV/cm) and excellent thermal and chemical stability. Baliga's figure of merit of β-Ga_2O_3 is 3214.1, superior to those of other materials such as GaN (846.0) or SiC (317.1). Although β-Ga_2O_3 is not a van der Waals material, β-Ga_2O_3 can be mechanically exfoliated from single crystal substrate into thin layer due to the large anisotropy of the unit cell. Quasi-2D β-Ga_2O_3 devices shows superior electrical properties and robustness in harsh environment, which shows potential of β-Ga_2O_3 as nanoscale power devices. However, quasi-2D β-Ga_2O_3 power devices show premature breakdown due to the electric field concentration. Adopting multiple field plates to relieve the electric field concentration and prevent premature breakdown greatly enhance the performance of power devices, which can be applied to β-Ga_2O_3 nanoelectronic power devices.

H-BN has been used as a dielectric material of 2D devices due to its excellent thermal conductivity and high dielectric constant, as well as atomically flat surface, which can be obtained through mechanical exfoliation. In our work, we used h-BN as a gate field plate dielectric layer by selective transfer on β-Ga_2O_3 channel using PDMS film. SiO_2 dielectric layer was deposited on devices followed by metal deposition for source field plate structure. By applying dual field plate structure, β-Ga_2O_3 devices can show excellent performance in high voltage condition.

β-Ga_2O_3 MESFETs with h-BN gate field plate were fabricated by using the β-Ga_2O_3 and h-BN flakes obtained from respective crystals. Ohmic metal was deposited on mechanically exfoliated β-Ga_2O_3 flakes, followed by precise positioning of exfoliated h-BN flakes on the channel. Gate field plate was fabricated with a part of the electrode overlapped with h-BN. Dual field plate structure was fabricated after deposition of SiO_2 and source field plate metal. Fabricated devices showed excellent output and transfer characteristics even after one month storage, which shows excellent air-stability. Three-terminal off-state breakdown voltage of fabricated device was measured, which shows improvement in breakdown voltage. The electric field distribution was calculated by Silvaco Atlas framework to study the effect of dual field plate on electric field, which explains the improvement of breakdown voltage in those structure. In this study, we present that the performance of β-Ga_2O_3 MESFET as a power device can be improved by adopting dual field plate structure, paving a way to the high-power nanoelectronic β-Ga_2O_3 devices. The details of our work will be discussed in the conference.

4:20pm **EM+2D+SS-WeA7 GaN Vertical Device Technology and its Future***, S.C. Chowdhury, **Dong Ji**,* UC Davis **INVITED**

Vertical GaN devices are ideal for high power applications owing to their wide bandgap-originated material properties, similar to SiC. What makes GaN vertical devices more attractive than SiC, is the capability to offer bulk regions with electron mobility over 1200cm^2/V·sec. Due to higher carrier mobility made possible by superior growth techniques, the figure of merit offered by GaN diodes or FETs is higher compared to SiC counterparts. From TCAD drift diffusion simulation we have shown the advantage of GaN devices become rapidly significant over SiC diodes at higher voltages. In our experimental studies we have successfully demonstrated transistors blocking over 1.4kV.

In this presentation, we will go over various types of vertical devices for power conversion that we are pursuing in our group and go over the achievements and challenges in each.

CAVETs were the first vertical devices[1] that demonstrated the potential of GaN in these technology. CAVETs are realized with Mg-ion implanted [2] current blocking layers (CBLs) with regrown channel. Alternatively they can have Mg-doped CBLs with a regrown channel layer on a trench. In our trench CAVETs we have successfully blocked up to 880V with an R_{on} less than 2.7milli-ohm cm^2.

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[1] **National Student Award Finalist**

To date, most successful results in GaN vertical devices have come out of MOSFETs, which traditionally rely on inversion channels. MOSFETs with an un-doped GaN interlayer as a channel and in-situ MOCVD oxide, called OG-FET have demonstrated superior performance with low specific on-state resistance (R_{on}) Over 1.4kV blocking with an R_{on} less than 2.2milli-ohm cm^2 was recently demonstrated by our group where the role of channel mobility got highlighted[3].

One of common issue in all these devices is the realization of a robust buried p-n junction, which we will also go over along with other challenges faced by each of these device types and discuss paths to overcome those.

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5:00pm **EM+2D+SS-WeA9 Effects of Proton Irradiation Energy on SiN_x/AlGaN/GaN Metal-insulator-semiconductor High Electron Mobility Transistors***, **Chaker Fares**, F.R. Ren,* University of Florida*; J.H. Kim,* Korea University, Republic of Korea*; S.J. Pearton,* University of Florida*; C.F. Lo, J.W. Johnson,* IQE*; G.S. Yang,* Korea University, Republic of Korea

The effects of proton irradiation energy ranging from 5 to 15 MeV on the electrical properties of SiNx/AlGaN/GaN metal-insulator-semiconductor high electron mobility transistors (MISHEMTs) using in-situ grown silicon nitride as the gate dielectric were studied. In applications such as satellite-based communication, remote sensing, radar technology, and nuclear energy production, microelectronics that are resistant to radiation must be utilized. Of the many materials and device architectures previously investigated, AlGaN/GaN high electron mobility transistors (HEMTs) show significant potential for environments where radiation hardness, elevated temperature, and high-power operation are required. Although several studies have been performed to analyze how HEMTs respond to irradiation damage, data on the effects of proton irradiation energy on MISHEMTs are scarce. In this study, AlGaN/GaN MISHEMT samples were irradiated at various proton irradiation energies at a fixed dose of 2.5×10^{14} cm^{-2} to determine the effects on device performance. After proton irradiation, all devices were functional and showed minimal degradation compared to previous reports of HEMTs irradiated at similar conditions.The dc saturation current was reduced by 10.4, 3.2 and 0.5% for MISHEMTs irradiated with proton energies of 5, 10, and 15 MeV, respectively. Device performance degradations were more pronounced in the irradiated samples under high-frequency operation. At a frequency of 100 KHz, the saturation drain current reduction at a gate voltage of 3 V was 40%, 19% and 17% after proton irradiation at 5, 10, and 15 MeV, respectively. At higher duty cycles, the drain current reduction is less severe. The results of this study demonstrated the device reliability of AlGaN/GaN MISHEMTs in environments where a resilience to radiation is required.

5:20pm **EM+2D+SS-WeA10 Cesium-Free III-Nitride Photocathodes Based on Control of Polarization Charge***, **Douglas Bell**,* Jet Propulsion Laboratory, California Institute of Technology*; E. Rocco, F. Shahedipour-Sandvik,* SUNY Polytechnic Institute*; S. Nikzad,* Jet Propulsion Laboratory, California Institute of Technology

III-nitride photocathodes are well-suited for ultraviolet (UV) detection, with commercial, defense, and astronomical applications. Photocathodes detect light by absorbing photons which create electron-hole pairs, and emitting those electrons into vacuum, where they are detected and amplified by a gain-producing device such as a microchannel plate. This type of device is capable of ultra-low dark current and enables photon counting. The wide bandgaps available in the AlGaN family provide intrinsic solar blindness, and the long-wavelength cutoff may be tuned by control of composition.

Among other properties, negative electron affinity (NEA) is desirable for these structures in order to maximize quantum efficiency (QE), or the number of electrons emitted per incident photon. Normally surface cesiation is used to create low or negative electron affinity of the GaN photocathode surface; however, the resulting highly reactive surface must be protected from air during fabrication and use, necessitating a sealed-tube configuration. Even so, the reactive surfaces of these devices cause degraded performance over time. Cesium-free photocathodes would offer lower cost, smaller size and mass, improved robustness, and greater chemical stability, in addition to the major advantages of higher QE and longer lifetimes.

We will report on the use of polarization engineering in order to achieve high QE without the use of Cs. We will discuss progress in design, fabrication, and characterization of polarization-engineered III-nitride photocathodes. An important component of these designs is the use of N-polar GaN and AlGaN. The nitride polarity affects the interface and surface polarization charge, and the ability to achieve low electron affinity depends critically on control of this charge. Designs using polarization charge engineering also enable optimization of the near-surface potential to further increase QE. We will describe the growth challenges of N-polar GaN and AlGaN and its implementation in photocathode devices. We will present results demonstrating high (>15%) QE for non-cesiated N-polar GaN photocathodes, with a clear path toward higher efficiency devices.

5:40pm **EM+2D+SS-WeA11 Current Enhancement for Ultra-Wide Bandgap AlGaN High Electron Mobility Transistors by Regrowth Contact Design***, **Erica Douglas**, B. Klein, S. Reza, A.A. Allerman, R.J. Kaplar, A.M. Armstrong, A.G. Baca,* Sandia National Laboratories

Recently, ultra-wide bandgap (UWBG) materials, such as Al-rich AlGaN with bandgaps approaching 6 eV, are being investigated to drive high-power electronic applications to even higher voltages, due to increased critical electric field compared to wide bandgap materials, such as GaN.[1] However, challenges have been encountered with Al-rich AlGaN, and in particular an increase in contact resistance as the bandgap for heterostructures increases.[2] High contact resistance ultimately limits the performance that can be achieved for these novel heterostructure-based devices, as source and drain resistances can be dominated by Ohmic contacts. While planar metal stacks with a rapid thermal anneal have shown some level of success, a complimentary approach using doped regrowth for the Ohmic contact regions with materials of lower bandgap has also shown a potential path for lowering contact resistance.[2] Our work explores regrown Ohmic contacts composed of lower bandgap Si-doped GaN to $Al_{0.85}Ga_{0.15}N/Al_{0.7}Ga_{0.3}N$ heterostructures , achieving a maximum saturated drain current of ~ 45mA/mm. Additionally, we demonstrate the ability to increase the saturated drain current almost 3X (from ~45 mA/mm to ~130 mA/mm) for UWBG HEMTs through a circular perforation design as well as a comb-type structure by means of regrowth contact design engineering.

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Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

6:00pm **EM+2D+SS-WeA12 Understanding Homoepitaxial GaN Growth***, **Jennifer Hite**, T.J. Anderson, M.A. Mastro, L.E. Luna, J.C. Gallagher, J.A. Freitas,* U.S. Naval Research Laboratory*; C.R. Eddy, Jr.,* U. S. Naval Research Laboratory

The availability of high quality, free-standing GaN substrates opens windows for new device applications in III-nitrides, especially in vertical structures. With the introduction of these native substrates, the properties of nitrides are no longer dominated by defects introduced by heteroepitaxial growth. However, additional materials challenges are coming to the forefront that need to be understood and surmounted in order to allow homoepitaxial devices to achieve their full potential.

In order to enable device-quality epitaxial layers, a deeper understanding of substrate preparation and the effects of the substrate and growth initiation on the characteristics of the epitaxial layers is required for metal organic chemical vapor deposition (MOCVD) growth of homoepitaxial films. We investigate these effects on epi morphology, uniformity, and impurity incorporation at the interface and in the films. Although the initial substrate factors influencing the epi can be subtle, they can have far reaching impact on device performance. Additionally, the interface between substrate and epitaxy is examined to enable reduction of unintentional impurity incorporation, especially Si, at this surface. By studying these effects using wafers from several different vendors, with substrates from both hydride vapor phase epitaxy (HVPE) and ammonothermal techniques, an understanding of the requirements for device quality MOCVD homoepitaxy can be determined.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-WeA

Theory and Dynamics of Heterogeneously Catalyzed Reactions

Moderator: Erin Iski, University of Tulsa

2:20pm **HC+SS-WeA1 Online Kinetics Study of Oxidative Coupling of Methane over La_2O_3 for C_2 Activation: What is Behind the Distinguished Light-off Temperatures***, **Yong Yang**, Z. Liu, E.I. Vovk, X. Zhou, C. Guan,* ShanghaiTech University, China

Oxidative coupling of methane (OCM) is a catalytic partial oxidation process that converts methane directly to valuable C_2 products (ethane and ethylene). The main difficulties from further investigation of this reaction are due to the nature of its high temperature and reaction exothermicity. In this work, a specially designed online characterization setup is applied for this reaction, which achieved both precise bed temperature control and real time product measurement. The setup combines a micro reactor and realtime mass spectroscopy. The reaction was performed under simulated industrial condition. For the first time, the Arrhenius plots of the major OCM products (CO_2, ethane and ethylene) were obtained, and their temperature dependence as well as the respective activation energy barriers were clearly differentiated, over a recently reported high performance nanorod La_2O_3 catalyst. Different from general expectation, CO_2, the fully oxidized carbon species, dominates all the products in the lower temperature region, and less oxidized C_2 species are only formed at much higher temperatures. Further analysis of the Arrhenius plots indicates that selectivity and apparent activation energy for both CO_x and C_2 products are strongly influenced by the oxygen concentration and temperature. Combined with density functional theory calculations and additional experimental measurements, significant insights are brought to this high temperature reaction of wide interest. Furtheranalysis specially focusing on this temperature region, applying XPS surface studies with *in-situ* high pressure cell and XRD bulk structure with *operando* reactor, revealed that there are both intermediates and poisoning species formation. With these new experiment results with distinguished lights-off products temperature provide new insights for understanding OCM reaction.

2:40pm **HC+SS-WeA2 Surface Reactivity of Activated CO_2***, **Richard van Lent**[1],* Leiden University, Netherlands*; A.J. Walsh, M.A. Gleeson,* DIFFER, Netherlands*; L.B.F. Juurlink,* Leiden University, Netherlands

Catalytically converting CO_2 into renewable fuels is a promising avenue that addresses the current fuel and energy storage challenges. Depending on the process, conversion of CO_2 may involve initial breaking of the OC=O bond. If so, this highly endothermic step is likely rate limiting to the overall process. Ultra–high vacuum (UHV) research on well-defined surfaces can provide fundamental insight into such processes, e.g. how dissociation may be aided by internal energy in CO_2, the metal's identity and the surface structure.

Internal energy has been shown to promote the highly activated dissociative adsorption of CO_2 on Ni(100) [1]. Rovibrationally state-resolved measurements for CH_4 on Ni(100) have shown that excitation of the ν_3 antisymmetric stretch vibration has a promoting effect that approximately equals kinetic energy for Ni(100) surfaces [2,3]. For other metal surfaces and CH_4 vibrations, the relative efficacy of vibrational and kinetic energies varies between 0.4 and 1.4 [2].

To start unravelling how CO_2 dissociates on a surface, we combine standard supersonic molecular beam techniques with high resolution continuous wave (cw) IR laser excitation. We study the effect of ν_3 antisymmetric stretch excitation of CO_2 on dissociative adsorption on a Ni(711) surface.

For excitation, we use a 3.9-4.6 µm single mode optical parametric oscillator (OPO). The OPO is frequency-stabilized by locking onto the derivative of the lamb dip of the specific rovibrational transition of interest. Frequency-stabilized IR radiation is crossed with a supersonic molecular beam that impinges onto the cleaned Ni(711) surface under UHV conditions. We use methods to determine absolute reactivities for CO_2 molecules with and without laser excitation. We extract rovibrational state-dependent absolute sticking probabilities as a function of kinetic energy. From this data, we determine the relative efficacy of vibrational and kinetic energy in overcoming the large activation barrier to dissociation.

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3:00pm **HC+SS-WeA3 Shining Light on Complexity: State- and Energy-Resolved Studies of Gas-Surface Reaction Dynamics and Mechanism***, **Arthur Utz**,* Tufts University **INVITED**

Gas-surface reactions on a metal surface can be far more complex than their net chemical equation would suggest. The heterogeneity of the surface, and its ability to restructure, impact the availability and energetics of reaction sites, energy redistribution processes triggered by the gas-surface collision dictate transition state access, and many coupled chemical processes can influence the reaction's outcome.

The talk will survey the ability to vibrational state selected measurements of gas-surface reactivity to systematically unravel important aspects of this complexity and provide molecular-level mechanistic insights that can guide our understanding and predictions about these processes. The experiments use infrared light to excite a single quantum rotational and vibrational level of the gas-surface reagent molecule and a molecular beam to define its incident kinetic energy. In this way, we are able to make energy-resolved measurements of reactivity while systematically varying the distribution of energy among the system's energetic degrees of freedom. Computational studies by our collaborators inform and guide our interpretation of the data.

Recent results will be featured and examine the impact of a vibrationally excited reagent molecule's symmetry on surface-induced energy redistribution, the quenching lifetime of a vibrationally excited molecule on a metal surface, the role of surface atom motion on reaction energetics, the ability to use these measurements to benchmark DFT electronic structure calculations, and how isolated surface structural features, including steps and adatoms, modify reaction energetics.

4:20pm **HC+SS-WeA7 Vibration-driven Reaction of CO_2 on Cu Surfaces via Eley-Rideal Type Mechanism***, **Junji Nakamura**, J.M. Quan, T. Kozarashi, T. Mogi, T. Imabayashi, K. Takeyasu, T. Kondo,* University of Tsukuba, Japan

We have long studied the formation of formate ($HCOO_a$) intermediates as an intermediates of methanol synthesis by hydrogenation of CO_2 on Cu surfaces [1-4]. It has been suggested based on the kinetic analysis for the high pressure bulb experiments that the formate formation proceeds via Eley-Rideal type mechanism, in which CO_2 directly reacts with adsorbed hydrogen atom on Cu. In order to clarify the mechanism and dynamics, we carried out CO_2 molecular beam studies with the translational energy of 1.12-1.97 eV and the nozzle temperature of 800-1100 K. It was found that hot CO_2 in the molecular beam reacts directly with pre-adsorbed hydrogen atoms on cold Cu(111) and Cu(100) surfaces at 120–220 K to form formate adspecies ($CO_2 + H_a \rightarrow HCOO_a$). That is, even at the low surface temperatures, formate species is formed rapidly when supplying energy only to CO_2. This indicates that the energy to overcome the reaction barrier comes from the hot CO_2 molecule itself instead of the Cu surface. The vibrational energy of CO_2 was much more effective for the reaction compared to the translational energy; and the reaction rate was independent of the surface temperature. The independence of surface temperature indicates the E-R type mechanism that the CO_2 molecule is not thermally equilibrated with the Cu surfaces but directly reacts with H_a. If the impinging CO_2 molecule chemisorbs on the Cu surfaces before reacting with H_a, the reaction rate should be dependent on the surface temperature, rather than the kinetic and the internal energies of CO_2. We evaluated the barrier distribution factors (*W*) of so-called Luntz equation by analysis of the reaction probability curves, which shows significant efficacy of the vibrational energy on the reaction of CO_2, which has not been observed before. DFT calculations are consistent with the experimental observations [5]. The direct reaction of CO_2 with adsorbed hydrogen atom can be regarded as the first example of vibration-driven bond formation reactions on surfaces.

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4:40pm **HC+SS-WeA8 First Principles Reaction Kinetics over Metals, Oxides and Nanoparticles***, Henrik Grönbeck,* Chalmers University of Technology, Gothenburg, Sweden **INVITED**

A major challenge in heterogeneous catalysis research is the determination of dominating reaction paths and kinetic bottlenecks. One reason for the challenge is the dynamic character of the kinetics, where the active sites may change with reaction conditions. Nevertheless, it is atomic scale information that allow for catalyst development beyond trial-and-error approaches. Kinetic modeling based on first principles calculations have over the past decade grown into an important tool for investigating the importance of different catalyst phases and reaction paths. In this contribution, I will discuss work where we have used density functional theory in combination with kinetic modeling to investigate catalytic reactions over metals, oxides and nanoparticles. The examples cover different aspects of kinetic modeling including determination of adsorbate entropies, importance of attractive adsorbate-adsorbate interactions and the complexity of many types of active sites.

Complete methane oxidation to carbon dioxide and water is used as one example and we have investigated the reaction over metallic Pd(100) and Pd(111) [1] as well as PdO(101) [2]. The reaction paths are shown to be markedly different on the metallic and the oxidized surfaces. We find that the catalytic activity is highly sensitive to adsorbate-adsorbate interactions which for PdO(101) are attractive owing to electronic pairing effects. This effect is crucial and common for oxide surfaces [3].

Reactions over platinum nanoparticles are investigated using a recently developed scaling relation Monte Carlo technique [4]. Taking CO oxidation as a model reaction, we find that the overall activity is determined by complex kinetic couplings. Effects of particle shape as well as internal and external strain will be discussed [5].

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5:20pm **HC+SS-WeA10 Formation of Pd/Ag Sandwiches, a Stable PdAg Subsurface Alloy, and the Pd Segregation induced by CO and O_2, Studied with STM, Ambient-pressure XPS, and DFT***, Matthijs van Spronsen,* Lawrence Berkeley National Laboratory*; K. Duanmu,* UCLA*; R. Madix,* Harvard University*; M.B. Salmeron,* Lawrence Berkeley National Laboratory*; P. Sautet,* UCLA*; C. Friend,* Harvard University

Efficient chemical production requires the use of materials able to selectively catalyze complex chemical reactions. High selectivity can be obtained by using noble metals. To improve activity, while retaining selectivity, small amounts of an active metal can be added. These species can function as active sites for, e.g., O_2 activation.

A promising alloy for selective hydrogenation is AgPd. The challenge using this material as a catalyst is the larger surface free energy of Pd, compared to Ag. This difference leads to Ag enrichment of the surface, hence, more Pd, both costly and scarce, is needed to ensure that Pd is present in the surface.

Here, the stability of Pd was probed in (sub)surface alloys formed by depositing sub-monolayer amounts of Pd on pure Ag single crystals, in order to evaluate the feasibility of using surface alloys as catalysts. These surface alloys would use much less Pd, but depend critically on understanding and control of the alloy composition and stability.

Mild annealing (~400 K) under ultra-high vacuum, leads to extensive migration of Ag and the formation of a Ag capping layer on the Pd. These measurements were based on scanning tunneling microscopy and X-ray photoelectron spectroscopy, supported by modeling (density functional theory). The etching, due to the loss of Ag, and the increase in island height, due to the capping, results in three-layer-high islands, covering both the terraces and the steps of the Ag(111) surface. The absence of significant amounts of Pd in the surface was confirmed by the lack of CO adsorption at 120 K.

The exposure of the Ag/Pd/Ag(111) surface alloy to gas atmospheres, either pure CO or O_2 (0.5 & 1 Torr, respectively), reverses the energetics, thus making Pd resurface. This was concluded from large core-level shifts observed in AP XPS measurements. Due to the proximity of Pd to the surface, the required temperature for Pd to segregate was rather low, in fact, for CO it was detected for 300 K. Resurfacing, and subsequent oxidation, of Pd was much slower, requiring cycling the temperature between 300 and 400 K in the O_2 atmosphere, several times. The difference stems from the fact that O_2 needs to be dissociated before it can form strong bonds to Pd, while CO can adsorb directly to Pd. The initial O_2-dissociation activity of the Ag-capped Pd is expected to be rather small.

To conclude, precise understanding of the stability of active metals with a high surface free energy is required to control the composition of surface alloys and its potential as active/selective catalyst.

Advanced Ion Microscopy Focus Topic
Room 203B - Session HI-WeA

Novel Beam Induced Material Engineering & Nano-Patterning

Moderators: Armin Gölzhäuser, Bielefeld University, Germany, Olga Ovchinnikova, Oak Ridge National Laboratory

2:20pm **HI-WeA1 Delving into the Finer Details of Helium FIBID***, **Frances Allen**,* University of California, Berkeley **INVITED**

Focused ion beam induced deposition (FIBID) of gaseous precursors enables localized template-free additive lithography at the nanoscale and is used in a range of applications, such as circuit edit in semiconductor engineering and the prototyping of nanodevices. To date, the majority of FIBID has used the gallium focused ion beam generated by the long-established liquid-metal ion source. However, with the development of the atomically sharp gas field-ionization source (GFIS) and subsequent emergence of the Helium Ion Microscope, FIBID using focused helium ion beams is increasingly of interest. The enhanced spatial resolution of helium FIBID over gallium FIBID and ability to deposit insulators free from gallium contamination are key areas of benefit.

The internal structure, composition, and overall shape of FIBID nanostructures and the influence of the deposition parameters thereon provide clues as to the growth mechanisms involved. Ultimately, the goal is to use this information to facilitate tunable FIBID in order to obtain nanostructures with a specific set of properties for a given application. I will present insights gleaned from scanning transmission electron microscopy (STEM) analysis of helium-FIBID nanostructures, where x-ray energy-dispersive spectrometry (XEDS) and new methods in "4DSTEM" diffraction are applied to obtain elemental compositions and grain orientation maps at the nanoscale with high sensitivity. The results are compared with those obtained for neon FIBID (the neon beam also generated by the GFIS source) and benchmarked against results from gallium FIBID. Several unique applications of helium FIBID drawing on the particular characteristics of helium-FIBID nanostructures will be discussed.

3:00pm **HI-WeA3 Anderson Localization of Graphene by Helium Ion Irradiation***, Y. Naitou, **Shinichi Ogawa**,* National Institute of Advanced Industrial Science and Technology (AIST), Japan **INVITED**

Graphene has been the subject of intensive research for its unique physical properties. Recently, tuning the electrical properties of graphene by irradiating it with an ion beam or exposing it to a reactive gas atmosphere has been of great interest[1][2]. The basic idea is to generate defects by using accelerated ion beam bombardment or reactive gas treatment and then to introduce localized states around the charge neutral point of graphene. Such localized states govern the transport properties of graphene, and highly defective graphene as a transition into a two-dimensional Anderson insulator is theoretically predicted[3].

Irradiation of a single-layer graphene (SLG) with accelerated helium ions (He^+) by helium ion microscopy (HIM) controllably generates defect distributions, which create a charge carrier scattering source within the

SLG. We report direct experimental observation of metal-insulator transition in SLG on SiO_2/Si substrates induced by Anderson localization. This transition was investigated using scanning capacitance microscopy by monitoring the He^+ dose conditions on the SLG. The experimental data show that a defect density of more than ~1.2% induced Anderson localization. We also investigated the localization length by determining patterned placement of the defects and estimated the length to be several dozen nanometers—no fewer than 20 nm and no more than 50 nm. These findings provide valuable insight for direct-patterning and designing graphene-based nanostructures using HIM. Further detail will be presented[4][5].

References

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[3] A. Lherbier et al. Phys. Rev. B 86, 075402 (2012).

[4] Y. Naito and S. Ogawa, Appl. Phys. Lett. 106, 033103 (2015)

[5] Y. Naito and S, Ogawa, Appl. Phys. Lett.108, 171605 (2016)

4:20pm **HI-WeA7 The Frontiers of Focused Ion Beam in Semiconductor Applications**, ***Shida Tan,*** Intel Corporation **INVITED**

The semiconductor performance scaling or "Moore's Law" has completely transformed the face of the planet and our daily life in the past half a century. This innovation trend continues through a combination of the transistor density scaling, heterogeneous integration, and architectural breakthroughs. These smaller critical device dimensions, thinner process layers, densely packed structures, complex device routing, and design architecture pose challenges to the focused ion beam (FIB) technology, which is used broadly in the entire product development cycle from the fabrication process to the final product debug and failure analysis. In this paper, we will talk about the unique advantages and applications of alternative ion beam in the areas of circuit edit, failure analysis, fault isolation, yield analysis, and mask repair. Trade-offs between various beam parameters to enable successful recipe implementation, challenges of the existing technologies, and the requirements for future instrumentation development will be discussed.

5:00pm **HI-WeA9 2D Materials Under Ion Irradiation: In-situ Experiments and the Role of the Substrate**, ***Gregor Hlawacek**, S. Kretschmer,* Helmholtz Zentrum Dresden-Rossendorf, Germany*; M. Maslov,* Moscow Institute of Physics and Technology*; S. Ghaderzadeh, M. Ghorbani-Asl, A.V. Krasheninnikov,* Helmholtz Zentrum Dresden-Rossendorf, Germany

Helium ion Microscopy (HIM) is frequently used for the fabrication of 2D nanostructures in graphene, MoS_2 and other materials. While some of the experiments are carried out with freestanding materials most of the work is done on supported material. While the defect production is understood for the former case, it is not fully understood in the latter setup. We used a combination of analytical potential molecular dynamics and Monte Carlo simulations to elucidate the role of the different damage channels, namely primary ions, backscattered atoms and sputtered substrate atoms.

Using this approach we looked at the defect production by helium and neon ions in MoS_2 and graphene supported by SiO_2 at typical energies used in HIM. We show that depending on ion species and energy defect production for supported 2D materials can be dominated by sputtered atoms from the support, rather than direct damage induced by the primary ion beam. We also evaluated the consequences of these additional damage mechanisms on the achievable lateral resolution for HIM based defect engineering and nano-fabrication in 2D materials. The obtained results agree well with experimental results obtained by in-situ and ex-situ characterization of defects in graphene and MoS_2.

5:20pm **HI-WeA10 Sample Heating Effects from Light Ions in Thin Films**, ***John A. Notte**, B.B. Lewis,* Carl Zeiss Microscopy, LLC

The term "FIB Renaissance" has been applied to the recent period of ion source development which has brought forth many new species suitable for focused ion beam (FIB) instruments. Several of the new species are relatively light ions, including hydrogen, helium, lithium, and neon, which are appreciably lighter than the prevailing gallium FIB – by a factor of 3 or more. At the conventional energies (5 to 30 keV) these ions species interact with the sample differently, and warrant a reconsideration of the established understanding which is largely founded on the traditional gallium FIB.

The most marked distinction of these light ions is the ratio of electronic stopping power compared to nuclear stopping power. For example, for a 30 keV helium ion, the nuclear stopping power can be a decade lower than its electronic stopping power. While for 30 keV gallium, the nuclear stopping power is a decade higher than the electronic stopping power. Consequential to this, near the surface the light ions remain relatively collimated because $M_{ion} >> M_{elec}$, making angular deflections necessarily small. As the light ions gradually penetrate deeper, they lose their energy, and the electronic stopping power is correspondingly reduced until the nuclear stopping power dominates. Here, large angular deflections become dominant, and the majority of the lattice damage takes place at these greater depths for light ions. For the special case of thin films, nuclear stopping might never become predominant for light ions.

The heat transfer mechanisms are even more drastically different when comparing light ions to heavier ions. First, by virtue of their large penetration depth, the light ions have a larger volume in which their energy is dissipated – reducing the corresponding temperature rise. But more significantly, the light ions lose most of their energy through excitations to the electrons. These excited electrons have characteristic mean free paths which can be relatively long, providing an effective pathway for energy transfer to a much larger volume. Whereas for nuclear stopping power, the ion's energy is transferred to the lattice much more locally. And since nuclear stopping is predominant for heavy ions, the energy is necessarily deposited locally, giving rise to appreciably higher temperature. Further, for the special case of thin films, the temperature rise from light ions is further reduced. Lastly, a special case of low beam currents is considered, where the time interval between ion arrivals may sometimes be longer than the time scale for thermal relaxation. This gives rise to non-overlapping temperature spikes which can be independent of probe current.

5:40pm **HI-WeA11 Helium Ion Direct Write Patterning of Superconducting Electronics**, ***Shane Cybart**, E.Y. Cho, H. Li,* UC Riverside*; Y. Naitou, S. Ogawa,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

We report the fabrication of nanoscale Josephson junctions in 25 nm thick YBa2Cu3O7 thin films. Our approach utilizes a finely focused gas field ion source from a helium ion microscope to directly modify the material on the nanometer scale to convert irradiated regions of the film into insulators. In this manner, the film remains intact and no material is milled or removed. We will present results of how the critical dimension beam affects the electrical properties. Furthermore we reflect on the potential of this method for future device applications in superconducting computing.

We acknowledge T. Iijima and Y. Morita for the usage of the HIM at SCR station of AIST.

MEMS and NEMS Group
Room 202B - Session MN+2D+AN+NS-WeA

IoT Session: MEMS for IoT: Chemical and Biological Sensing

Moderators: Robert Davis, Brigham Young University, Sushma Kotru, The University of Alabama

2:20pm **MN+2D+AN+NS-WeA1 BioMEMS for Eye Applications**, ***Yu-Chong Tai,*** California Institute of Technology **INVITED**

The field of Micro-Electro-Mechanical Systems (MEMS) has advanced tremendously for the last 20 years. Most noticeably, however, the field has mostly advanced in microsensors such as pressure sensors, accelerometers, gyros, microphones for cell phone and smart instrumentation applications. Looking forward though, in my opinion, one future direction of MEMS/NEMS is for micro biomedical devices. Among many possible biomedical applications, one challenging but promising branch is micro implants. Why micro implants? Body tissues (especially neurons), once severely damaged, do not repair or regenerate easily and often leave behind permanent debilitating deficits. Engineering implant technologies to interface intact tissues and/or to replace defective functions have continued to be the main solutions for many diseases. As our world is facing more severe aging population problems, significant growth in implant applications is foreseeable. As a matter of fact, there are already many existing commercially available implants such, as pacemakers and cochlear implants, but they all have a lot to improve. For examples, cardiovascular implants like defibrillator and pacemakers are still bulky, mechanically rigid, power hungry, and functionally limited. The future implants should be even smaller, flexible, power efficient and more versatile so that they can be used at places not possible before. This talk will review the research of implants done at the Caltech MEMS lab. More specifically, this talk will focus on bioMEMS implant devices to treat eye diseases. Examples of devices will cover the four major ophthalmic diseases, i.e., cataract, glaucoma, age-related macular disease and diabetic retinopathy that make of close to 80% of world blindness. It is believed that BioMEMS can also have many other opportunities for other organs in our body too.

3:00pm **MN+2D+AN+NS-WeA3 Real-Time, Single Cell, Size Measurements using a Facile, Multimode Microwave Resonator***, **Selim Hanay**, H. Aydogmus, A. Secme, H.S. Pisheh, M. Kelleci, U. Hatipoğlu,* Bilkent University, Turkey

In this study, a facile microwave sensor is designed and fabricated to detect transient cells one by one and extract their morphological and electrical properties in real time, without labeling. Multiple modes can be measured by multiplexing the electronic frequencies to obtain multiple analytic parameters at the same time. Our simple fabrication technique obviates the need to complex fabrication process.

A microwave sensor, in the form of a microstrip line resonator, is constructed by fixing copper tape at the back and the front side of a 1-mm thick glass slide. The backside is covered entirely with the tape to form a ground plane; on the front side, a copper tape was thinned within a few mm, extended across the slide and terminated with SMA feed through. On the front side, just below the copper tape, five capillary tubes are placed to transport the cells into the active sensing region. Microwave signals are transmitted through the two SMA ports at the end of the glass slide, perpendicular to the flow. The resonator is formed by electrically shorting the input/output ports. An initial characterization of the device is done by using spectrum analyzer so that its first and second order mode frequencies are obtained.

A digital phase-locked loops (PLL) measurement system with PI controller was constructed to track the resonance frequencies of the first two modes simultaneously in real-time. The PLL system tracks the two modes of the microstrip line resonator to sense the frequency shifts originating from the passage of the cells in the capillary.

As a proof of concept, initial PLL measurements were done with DI water. As water flows through the tube, frequency shifts around 100 kHz were observed in both modes. Later on, wildtype *Skbr3* breast cancer cells were flown through the same capillary. Frequency shifts in both modes were the responses of the resonator to the passage of the *Skbr3* cells beneath microstrip-line. The ratio between the first and second mode frequency shifts can be used determine the location of each cell by two-mode theory. The analyzed data indicates almost a constant slope, verifying the positional response of the sensors. Moreover, the size distribution of the cells is cumulated around a contour line for constant size as expected.

Earlier, we had detected single cells and distinguished different oncogenic cell lines using a PDMS based device. With this work, single-cell detection and sizing are accomplished with a device paradigm that does not require any lithography, metal deposition under vacuum or precise alignment of electrodes.

We acknowledge funding from European Research Council (ERC) Starting Grant (REM, 758769).

4:20pm **MN+2D+AN+NS-WeA7 Magnetic Microsystems for Communications***, **Rob Candler**,* University of California at Los Angeles **INVITED**

We are witnessing a rapid expansion of embedded devices (IoT) that have a variety of functions but a common requirement, to communicate with one another. These devices will be connected on a scale previously unseen, and they will therefore require an approach to efficiently generate and receive electromagnetic waves in a small form factor. One such approach is to rethink the way electrically small antennas operate, shifting from a current-based antenna to a voltage-controlled multiferroic antenna. Multiferroics are material systems with coupled magnetic and electrical properties, and they offer a new route for the miniaturization of magnetic field-coupled devices. Multiferroic systems allow for the conversion of magnetic flux to a voltage (and vice versa) without the need of a wire loop, avoiding inefficiencies due to Ohmic loss. *In particular, strain-coupled heterostructures* of magnetostrictive and piezoelectric materials have received much attention, as they can offer magneto-electric coupling many order of magnitudes higher than found in single-phase materials. A rapidly emerging research space in multiferroics is the development of miniature wireless devices, such as antennas and energy harvesters, taking advantage of the efficient flux-to-voltage conversion of multiferroics. In this talk, I will present work showing the impact of multiferroic coupling on the ferromagnetic resonance in GHz Bulk Acoustic Wave resonators, as well as investigations in frequency mixing from non-linear multiferroic affects. These results are all in support of our goal create a microscale multiferroic antenna that is orders of magnitude more efficient than its classical antenna counterpart.

Furthermore, continued miniaturization of existing and emerging components that use magnets (atomic clocks, quantum computing, magnetic memory) will increase their sensitivity to external magnetic fields as well as the crosstalk between components. To address this need, we are developing techniques for on-chip magnetic shielding using multiple layers of permalloy. We will present recent results showing microscale magnetic shields fabricated by electroplating multiple permalloy layers into molds, as well as milliscale shields that were conformally electroplated on 3D printed sheaths.

5:00pm **MN+2D+AN+NS-WeA9 MEMS-Based Resonant Sensors for IoT Applications***, **Oliver Brand**, M. Kim, P. Getz,* Georgia Institute of Technology **INVITED**

The presentation discusses resonant microsensors, in which the measurand affects a characteristic of the resonance behavior of a resonant microstructure or a resonant circuit, such as its resonance frequency or quality factor. Resonant sensing is a very versatile sensing approach and can be adapted to a large variety of physical, chemical and biological measurands. Especially when using the resonance frequency as the sensing signal, high resolution is achievable since frequencies can be measured accurately. The presentation will highlight two possible implementations of resonant chemical sensors for Internet of Things (IoT) applications, a cantilever-based electromechanical resonator and a purely electrical L-C resonance circuit.

The first example is an electro-mechanical resonant chemical sensor based on a silicon hammerhead structure coated with a polymeric sensing film for the detection of volatile organic compounds. The presentation will highlight how proper selection of the resonance mode, in this case an in-plane vibration mode, and device geometry can improve device performance and how fast temperature modulations of the resonant sensors enable the observation of signal transients that contain additional analyte information. The sensors are fabricated using a CMOS-compatible bulk-micromachining process, have resonance frequencies between 400-800kHz and achieve sub-ppm limits of detection for select analytes.

The second example is a purely electrical resonant chemical sensor in form of a flexible and stretchable L-C (inductor-capacitor) sensor, which is battery free and can be wirelessly interrogated. To achieve stretchable sensor characteristics, the spiral inductor and interdigitated capacitor structures are formed by a liquid metal, eutectic gallium-indium (EGaIn). A subtractive reverse stamping technique is used to form the conducting liquid metal lines with dimensions as small as 2µm inside PDMS microchannels and a 3D heterogeneous integration technique is applied to vertically stack and electrically interconnect the capacitor and inductor structure. Liquid and gaseous analytes change the capacitance and are detected by wirelessly measuring the resonance frequency of the L-C circuit around 143MHz.

5:40pm **MN+2D+AN+NS-WeA11 Etched Silicon Microcolumn For Tunable Thermal Gradient Gas Chromatography***, **Aaron Davis**, P. Schnepf, P.S. Ng, R.R. Vanfleet, R.C. Davis, B.D. Jensen,* Brigham Young University

The connection of the digital and physical world will be strengthened by chemical sensors that can measure complex mixtures of molecules. Gas chromatography is the gold standard for identification of volatiles and gases. Conventional gas chromatography systems have unparalleled resolution, but are large and power intensive. Microcolumn gas chromatographs are more portable but have dramatically reduced resolution. Combining the resolution of conventional systems with the size factor of micro systems is important for improving the affordability and portability of high performance gas analysis. Recent work has demonstrated feasibility of high resolution separation of gases in a benchtop-scale short-column system by controlling thermal gradients through the column. In order to further decrease the size of a gas chromatography system, microfabrication techniques were used to demonstrate the fabrication of a thermally controllable micro-scale gas chromatographic column with a small footprint (3 cm square). To fabricate microcolumns we are using deep-reactive-ion-etching, nickel evaporation, and wafer bonding. The design of the 20 cm column utilizes 21 individually controllable thin film heaters and solid conduction cooling to produce the desired thermal profile.

Nanometer-scale Science and Technology Division
Room 203A - Session NS+MN+PC+SS-WeA

IoT Session: Bio at the Nanoscale

Moderators: Juraj Topolancik, Roche Sequencing Solutions, Liya Yu, NIST Center for Nanoscale Science and Technology

3:00pm **NS+MN+PC+SS-WeA3 Nanoscale Label-free Imaging of Protein Molecules via Photo-induced Force Microscopy***, D. Nowak,* ***Sung Park,*** Molecular Vista

Nanoscale real space imaging of biological and biomaterial surface is not straightforward even with advances in microscopy techniques. Photo-induced Force Microscopy (PiFM) [1] combines infrared (IR) absorption spectroscopy and atomic force microscopy (AFM) via illumination of the tip-sample junction with tunable IR laser light and mechanical detection of forces acting on the tip in response to absorption of light by the sample. By mapping the IR absorption of the sample as a function of IR wavelength and position, nm-scale resolution is achieved in displaying the locations of heterogeneous materials on the surface of a sample. For protein molecules, amide I and II bands are readily accessible via tunable quantum cascade laser and provide ways to interrogate the molecule's local chemical environment. PiFM can provide both high resolution spectral imaging at a fixed wavenumber and full PiFM spectrum (analogue to FTIR spectrum) with a spectral resolution of 1 cm^{-1} and spatial resolution of sub-10 nm. Results on collagen molecules, individual icosahedral protein cages, and nanoparticle/protein systems will be presented.

[1] D. Nowak et al., Sci. Adv. **2**, e150157 (2016).

3:20pm **NS+MN+PC+SS-WeA4 Evaluating Reaction-diffusion Immunoassays via High-resolution Imaging Techniques***,* ***Imanda Jayawardena,*** University of Queensland, Australia*; S. Corrie,* Monash University, Australia*; L. Grondahl,* University of Queensland, Australia

Immunodiffusion is a simple assay used for the determination of a target protein concentration in a biological sample using a distance-based measurement. The assay allows the sample containing the antigen of interest to combine with an antiserum in a gel-based substrate leading to the formation of a ring-shaped precipitate ('precipitin ring'), the size of which is proportional to target protein concentration.[1] Using the malarial antigen HRP2 and antisera from immunized rabbits as the model system, for the first time, we are investigating transforming the current immunodiffusion assays into a more rapid and sensitive format.

The traditional assay substrate, agarose, is a severely diffusion limited system. The porosity of the gel is a key determinant of diffusion properties and is an essential parameter required for the study and modification of the assay. However, the scientific data on agarose pore size determination is based on artefact laden microscopy images of agarose hydrogels. Thus, we have performed an in-depth investigation on best imaging techniques for accurate pore size determination. The precipitin ring structure is a band of antigen-antibody precipitate, in significant contrast with the surrounding gel substrate. A brief preliminary investigation has been reported by Fedorov et al. on precipitin ring structure[2], and we have extended this work by applying microscopic imaging techniques.

For imaging hydrogels, high pressure frozen gels were subjected to cryo-SEM[3], and was established as the most accurate technique to study the native structure of the gel. Atomic force microscopy was found to complement cryo-SEM data while CLSM due to its limited resolution was found to be inadequate for the imaging of hydrogels. For imaging the protein-rich precipitin ring structure, high pressure frozen ring sections were subjected to cryo-SEM, however, more meaningful insight on the ring structure was obtained in this instance through CLSM studies.

Herein, we aim to present our work described above on imaging agarose hydrogels for accurate pore size determination and imaging precipitin ring structures associated with immunodiffusion assays.

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2. Fedorov, A. A.; Kurochkin, V. E.; Martynov, A. I.; Petrov, R. V. *Journal of Theoretical Biology* **2010**
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4:20pm **NS+MN+PC+SS-WeA7 The Last Nanometer – Hydration Structure of DNA and Solid Surfaces Probed by Ultra-High Resolution AFM***,* ***Uri Sivan****, K. Kuchuk, I. Schlesinger,* Technion - Israel Institute of Technology, Israel **INVITED**

Recent advancements in atomic force microscopy facilitate atomic-resolution three-dimensional mapping of hydration layers next to macromolecules and solid surfaces. These maps provide unprecedented information on the way water molecules organize and bind these objects. Since the hydration structure governs the energetics of solvation and interactions between objects immersed in solution, the new data are invaluable when trying to resolve fundamental questions such as identification of molecular binding sites and interaction mechanisms.

After a short presentation of our home-built microscope, characterized by sub 0.1 Å noise level, the talk will focus on two representative studies. The first one will disclose our recent finding that in solutions in contact with atmosphere, hydrophobic surfaces are generically coated with a dense layer of adsorbed gas molecules. This layer renders the hydrophobic interaction a certain universality, regardless of the underlying surface. The second study will present our recent success in obtaining ultra-high resolution images of DNA and 3d maps of its hydration structure. This study shows that labile water molecules concentrate along the DNA grooves, in agreement with known position of DNA binding sites.

5:00pm **NS+MN+PC+SS-WeA9 Open-hardware, High-speed Atomic Force Microscopy using Photothermal Off-resonance Tapping***,* ***Georg Fantner,*** École Polytechnique Fédéral de Lausanne, Switzerland **INVITED**

Self-assembly of protein complexes is at the core of many fundamental biological processes. To reach a comprehensive understanding of the underlying protein self-assembly reactions, high spatial and temporal resolution must be attained. This is complicated by the need to not interfere with the reaction during the measurement. Since self-assemblies are often governed by weak interactions, they are especially difficult to monitor with high-speed atomic force microscopy due to the non-negligible tip-sample interaction forces involved in current methods. Here we develop a high-speed atomic force microscopy technique, photothermal off-resonance tapping (PORT), which is gentle enough to monitor self-assembly reactions driven by weak interactions. Using photothermal actuation on ultra-small HS-AFM cantilevers we perform force-distance curves at two orders of magnitude higher rates than in conventional off-resonance methods. From the time-domain tip sample interaction we extract tip-sample force curves to quantify the *"static"*forces due to the cantilever deflection, and the *"impact"* forces due to the rapid deceleration of the cantilever tip upon impact. Experimental characterization of the tip-sample forces in HS-tapping mode-AFM and PORT revealed that imaging forces in PORT are less than 1/5thof those exerted in conventional HS-AFM.

One of the key enabling factors for PORT is the real time control of the cantilever position using photothermal excitation. This requires low level, control of the feedback architecture and optimized AFM instrumentation. I will discuss the relevant components developed in my laboratory and explain how we share them with the broader scientific community using an open-hardware scheme.

We apply PORT to dissect the self-assembly reaction of SAS-6 proteins, which form a nine-fold radially symmetric ring-containing structure that seeds formation of the centriole organelle present in all eukaryotic cells. Using machine learning algorithms we traced hundreds of molecules over time to extract reaction kinetics from single molecule interactions. These measurements show that 9-fold closed SAS-6 rings are under pre-tension in their natural state. Due to the high temporal and force resolution provided by PORT, we found that, contrary to the current belief, more than one assembly route exists to reach the nine fold symmetry. These observation resets our current thinking about the assembly kinetics of this crucial step in cell replication.

5:40pm **NS+MN+PC+SS-WeA11 Development of Multimodal Chemical Nano-Imaging for *in situ* Investigations of Microbial Systems***, A. Bhattarai, B.T. O'Callahan, P.Z. El Khoury,* ***Scott Lea,*** Pacific Northwest National Laboratory*; K.-D. Park, E.A. Muller, M.B. Raschke,* University of Colorado Boulder

Existing genomic and biochemical methods cannot directly probe the physical connections involved in microbial metabolic processes over relevant length scales, spanning the nano-meso-micrometer spatial regimes. Determining the location and function of such biomolecules would aid in identifying the mechanisms governing microbial interactions. We are addressing these technical and conceptual gaps by developing a single multimodal chemical imaging platform that can interrogate biomolecules in living systems using three complementary label-free, nanoscale, ultrasensitive chemical imaging techniques:

Infrared scattering scanning near-field optical microscopy (IR *s*-SNOM)

Tip-enhanced Raman nano-spectroscopy (TERS)

Multimodal hyperspectral optical nano-spectroscopy.

We have built and developed these imaging modalities independently prior to integration into a single, multimodal chemical nanoscope. As part of our benchmarking experiments, we performed TERS measurements targeting prototypical systems and constructs and demonstrated <1 nanometer precision in ambient TERS chemical imaging measurements.[1] We also established an overall broader scope of TERS[2] and illustrated that TERS is not restricted to nanoscale chemical imaging, but can also be used to probe different aspects of local fields confined to a few nanometers. Our new setup, equipped with a hyperspectral imager, enables hyperspectral fluorescence, optical absorption, dark-field scattering, Raman scattering, and topographic imaging. Recently, we used this capability to visualize pigments in lipid monolayers and within a single live *T. lutea* cell in solution.[3] For IR *s*-SNOM, we are working on developing an AFM capable of bottom illumination and collection of IR light to support measurements in aqueous environments. The approach would use a piezoelectric scanner mounted ZnSe prism to enable evanescent wave illumination and collection of scattered IR light. We are also benchmarking the IR *s*-SNOM with the TERS and hyperspectral imaging modalities on a number of model biological systems including bacteria, collagen, and cytochromes.

This unique AFM-based instrument could be used to investigate a wide range of biomolecules through their characteristic electronic and vibrational signatures, over the nano-meso-micrometer scales. This platform will not only enable recording chemical images of single microbial cells at the subcellular level, but it will also enable mapping entire microbial communities with chemical selectivity.

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Plasma Biology, Agriculture, and Environment Focus Topic
Room 104A - Session PB+BI+PC+PS-WeA

Plasma Agriculture & Environmental Applications

Moderator: Deborah O'Connell, University of York, UK

2:20pm **PB+BI+PC+PS-WeA1 Pulsed Power Applications for Farming and Food Processing***, **Koichi Takaki**,* Iwate University, Japan **INVITED**

High-voltage and plasma are useful in several stages in agriculture, fishery and food processing including contribution to the food safety. Pulsed high-voltage produces intense high-electric field which can cause some biological effects such as stress response (stimulation) and electroporation. Types of pulsed power that also have biological effects are caused with gas discharges and water discharges which include reactive species such as ROS and RNS. We developed repetitively operated compact pulsed power generators with a moderate peak power for the agricultural applications.

The pulsed repetitive discharge were used for promoting growth of the vegetables and fruits. The growth rate of the vegetables and sugar content in the strawberry harvested after the cultivation increased by the plasma irradiation to the hydroponic solution [1] . The plasma was irradiated in the drainage water for 10 and 20 minutes each day. The leaf size of the plants increased with plasma treatment time. Number of colony forming units (CFU) of *R. solanacearum* in the liquid fertilizer decreased from 10^7 to 10^2 CFU/mL using the discharge plasma treatment [2]. Seedlings with discharge plasma treatment were relatively healthy; in contrast, all seedlings in the positive control wilted and died from infection of *R. solanacearum* after 12 days. The yielding rate of Shiitake mushroom (*L. edodes*) was also improved with the high-voltage stimulation in fruit-body formation phase [3] .

Electrostatics effect were used for keeping freshness of not only agricultural products [4, 5], but also marine products [6] . In postharvest phase of agriculture, keeping freshness in storage house and in transportation container is important. The electrostatic effects can contribute to remove airborne bacteria and fungi spore from the storage house and container [4] . This removal contributes to reduce the infection risk with fungi and bacteria. Some kinds of fruit and vegetable emit the ethylene gas which accelerate a degradation of other kind fruits and vegetables. The plasma can contribute the ethylene removal via oxidization reaction [5] . The AC electric field induces a conformational change of protein. This technologies can contribute to extend the freshness of marine products [6] .

References:

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3:00pm **PB+BI+PC+PS-WeA3 Stimulus Control on Organisms Using Pulsed Power Technology***, **Douyan Wang**, T. Namihira,* Institute of Pulsed Power Science, Kumamoto University, Japan **INVITED**

Pulsed power is instantaneous ultra-high power with high energy density (10^5-10^7J/m^3). By controlling and utilizing it in a narrow space and an instantaneous time, phenomena and reactions that are not attained by conventional and ordinary methods can be achieved. For instance: electromagnetic field, discharge plasma, shockwaves, intense light emission, etc. By selecting or combining some of these physical phenomena, it is able to control the degree of output performance. Bioelectrics refers to the use of pulsed power, powerful pulsed electric or magnetic field for extremely short periods of time, non-thermal plasmas in gases or liquids and shock waves, in order to give novel physical stresses to biological cells, tissues and/or organisms as well as bacteria. Bioelectrics is an interdisciplinary academic field over physics, chemistry, biology, medical science, agriculture, environmental, mechanical and electrical engineering, and is expected to open up new science and technology.

By controlling the degree of electrical stimulations using pulsed power, it is possible to either inactivate biological targets or keep them alive and activate their functions. Examples of inactivation are given as: sterilization of liquids, treatment of algae and marine harmful organisms, growth inhibition of plants. On the other hand, more delicate stress control enables the activation of living organisms such as transcriptional activation of genes, substance transduction into cells, growth enhancement of plants. Both direct and indirect stimuli are useful. Here, aerial, liquidus and edaphic environmental control are examples of the indirect stimulus.

4:20pm **PB+BI+PC+PS-WeA7 Synthesis of Nitrates by Atmospheric Microplasma in Aqueous Solution***, **Nicolas Maira**, F. Reniers,* Université Libre de Bruxelles, Belgium

For many years, cold atmospheric plasma techniques have been used for a large variety of applications such as surface modification, film deposition, nanoparticles synthesis or pollutants degradation. One of their main advantage is the possibility to work with a gaseous, liquid or solid phase. In this study, the plasma water treatment is investigated for a potential application in agriculture. When water solutions are treated by plasma, in air environment, several reactive oxygen and nitrogen species (RONS) are generated [1,2]. The main RONS are hydrogen peroxide (H_2O_2), nitrites (NO_2^-) and nitrates (NO_3^-). Nitrates are one of the most essential molecules for plants because, together with ammonium, they represent an important source of nitrogen which is mandatory for DNA, RNA, enzymes, chlorophyll, ATP and many other molecules. For some applications such as hydroponics or urban agriculture, the local production of pure nitrates fertilizers directly available in the flowing water feeding system would be of great interest.

In this study, a DC atmospheric microplasma system is used for the investigation of the formation mechanism of NO_3^- in water. The liquid phase is analyzed by Ionic Chromatography (IC), UV-visible spectrometry (UV-vis) and pH-metry, whereas the gas phase is probed by Optical Emission Spectroscopy (OES) and atmospheric Mass Spectrometry (MS).

Firstly, the influence of the inner diameter of the microplasma stainless steel needle is investigated (internal diameter of 0,76 mm, 0,50 mm and 0,20 mm). The amount of NO_x^- (NO_2^- and NO_3^-) synthesized varies with the diameter and the shape of the plasma is different for a larger internal diameter. Furthermore, the total amount of NO_x^- formed in a solution shows a linear trend with the total charge injected into the plasma with, however different slopes for nitrites and nitrates.

The oxidation mechanism of NO_2^- to NO_3^- is then explored and the influence of other reactive species on this mechanism is then studied. Indeed, it is known from the literature that H_2O_2 may play a role in the process for different atmospheric plasma systems [2]. The formation of oxygenated water and its role as an oxidant is highlighted in the microplasma system.

Therefore, the amount of H_2O_2 synthesized by microplasma is compared to other plasma systems. The nature of the atmosphere above the solution is modified in order to determine the species formed in the gaseous phase and their respective influence.

The authors would like to thank the financial support of NITROPLASM (EOS Project 30505023)

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5:00pm **PB+BI+PC+PS-WeA9 Design Considerations for Plasma-based Water Purification Reactor Scale-up**, ***John Foster**, S.M. Mujovic, J.R. Groele, J.C.Y. Lai,* The University of Michigan-Ann Arbor **INVITED**

Plasma-based water purification has been proven viable in laboratory demonstration experiments, highlighting its effectiveness at the removal of contaminants of emerging concern and at disinfection. While these small scale experiments bolster the promise of plasma based advanced oxidation, translating demonstration experiments to practice has proven challenging. A chief challenge is the scale up of plasma-based methods to a viable water treatment technology that is both robust and usable at treatment flow rates of interest. Presented here is an attempt to frame the scope of the challenge, the current state of the art in plasma water purification, and scale up design considerations both from plasma science and engineering standpoints. The objective here is to summarize key challenges to scale-up and implementation as well as elaborate on approaches to achieving a high throughput plasma-based water treatment system. Two illustrative reactor examples amenable to scale up are highlighted along with associated performance data. The pathway from bench-top demonstration of plasma-based systems to piloting and ultimately to the reduction of the technology to practice is also elaborated upon.

5:40pm **PB+BI+PC+PS-WeA11 Radicals and Ozone Generated in Ar/He and Ar/He/H_2O Plasma by using Atmospheric Pressure Plasma Jet Systems and their use in Methylene Blue Degradation**, *J.H. Hsieh, **YiJinWei Wei**,* Ming Chi University of Technology, Taiwan, Republic of China*; C. Li,* National Yang Ming University, Taiwan, Republic of China

Optical emission spectroscopy (OES) and UV absorption spectrometry were first used to gather information about the excited species present near/in the plasma plume generated using Ar/He and Ar/He/H_2O gases with an atmospheric pressure plasma jet (APPJ). Afterward, the APPJ system was used to study its efficiency in degrading methylene blue as a function of radical and ozone density. According to the results, it was found that the degradation of methylene blue was directly related to the ozone concentration and, perhaps, OH radical density. Additional moisture may be used to control the ratio of ozone and OH radical density, resulting in the variation of degradation rate. Complete degradation of MB can be achieved in 80 seconds.

Plasma Science and Technology Division
Room 104C - Session PS+EM-WeA

Advanced BEOL/Interconnect Etching

Moderators: Michael Morris, Trinity College Dublin, Tetsuya Tatsumi, Sony Semiconductor Solutions Corporation

2:20pm **PS+EM-WeA1 Etch Strategies for Reducing Defects and Pattern Roughness in BEOL EUV Patterning**, ***Jeffrey Shearer**,* IBM Research Division, Albany, NY*; A. Raley, Q. Lou, J. Kaminsky,* TEL Technology Center, America, LLC*; L. Meli,* IBM Research Division, Albany, NY

As EUV lithography takes center stage in next-node semiconductor logic manufacturing, many challenges still need to be overcome. Of those, resist scumming, resist line breaks, and pattern roughness stand out as three of the top issues to address, especially when direct printing single levels below 36nm pitch. Previously, we have reported several methods of addressing these concerns in BEOL patterning, including introducing new material stacks and implementing new etch techniques such as resist reinforcement and quasi-atomic layer etching (QALE). This presentation will expand upon those ideas as well as introduce new etch methods that help enable direct EUV printing of single levels. Resist scumming will be addressed by exploring different types of descum etch chemistry. Data will show that line breaks can be reduced by resist reinforcement methods using pre-etch in situ deposition, increasing etch selectivity using QALE, and implementing direct current superposition (DCS). Additionally, we will show how line end pullback can be modulated with these different techniques and data will be presented that show resist reinforcement methods can recover more than 50% of line end pullback caused by more selective etch chemistries. The aspect ratio dependence of resist reinforcement and QALE will be discussed along with how aspect ratio impacts pattern roughness. The effectiveness of all of these etch strategies will be evaluated with defect characterization (bridge patterns and line breaks) and electrical testing (shorts and opens yield). Finally, we will discuss the impact of chamber configuration on EUV lithography pattern transfer. Data will be shown from chambers with the radio frequency (RF) split between top and bottom electrodes, dual RF on the bottom electrode only, and RF split between top and bottom electrodes with the addition of DCS. This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

2:40pm **PS+EM-WeA2 Influence of Topological Constraints on the Ion Damage Resistance of Low-*k* Dielectrics**, ***Qing Su**,* University of Nebraska-Lincoln*; T. Wang, J. Gigax, L. Shao,* Texas A&M University*; W. Lanford,* University at Albany*; M. Nastasi,* University of Nebraska-Lincoln*; L. Li,* Intel Corporation*; G. Bhattarai, M.M. Paquette,* University of Missouri-Kansas City*; S.W. King,* Intel Corporation

Low-*k* dielectric materials are well known to be sensitive to process induced damage during back-end-of-line (BEOL) patterning and metallization. This sensitivity has been largely attributed to the incorporation of terminal organic groups into the structure of low-*k* dielectric materials to lower dielectric permitivity and the subsequent loss of the terminal organic groups during BEOL processing. However, the correlations between the actual atomic structure of low-*k* dielectrics and their susceptibility to BEOL damage have been largely qualitative. A more quantitative metric for relating both the atomic structure and network topology of low-*k* dielectrics to downstream processing would allow for more efficient design and selection of materials for BEOL as well as pitch division multi-pattern applications.

Toward this end, we have investigated the ion radiation damage resistance for a series of low-*k* and high-*k* dielectric amorphous hydrogenated silicon carbide (a-SiC:H) thin films, wherein atomic structure and topological constraints have been previously shown to play a remarkably fundamental role in determining the full spectrum of electrical, optical, thermal, and mechanical properties. We specifically show the response of a-SiC:H films with > 37% hydrogen content and mean atomic coordination ($<r>$) ≤ 2.7 subjected to 120 keV He^+ irradiation with damage level to 1 displacment per atom (dpa). Significant hydrogen loss, bond rearrangement, and mechanical stiffening were induced in these films. In contrast, comparatively minor changes were observed for a-SiCH films with <35% hydrogen content and $<r> > 2.7$ also exposed to the same He^+ irradiation. The observed radiation hardness threshold at $<r>_{rad} > 2.7$ is above the theoretically predicted rigidity percolation threshold of $<r>_c = 2.4$. As we will show, the higher observed radiation hardness threshold can be interpreted as evidence that terminal hydrogen bonds and bond bending forces associated with two-fold coordinated motifs are too weak to function as constraints in collisions with high energy ions. Eliminating these constraints from consideration would increase $<r>_c$ to > 2.7 in agreement with the observed $<r>_{rad} = 2.7$. These results demonstrate the key role of network coordination and topological constraints in ion damage resistance and perhaps provides new criteria for the design of new ion damage resistant / tolerant materials.

3:00pm **PS+EM-WeA3 BEOL Patterning Challenges for 14nm and Beyond High Volume Manufacturing**, ***Xiang Hu**,* GLOBALFOUNDRIES*; Y. Ren,* GLOBALFOUDRIES*; D. Medeiros, P. Lee,* GLOBALFOUNDRIES **INVITED**

As the semiconductor features progressively shrink to sub 20 nm dimensions, patterning technology becomes significantly more critical. Pattern fidelity, yield, quality and cost now all incrementally become competing factors to the successful production of advanced technology nodes in high volume manufacturing. In this paper we will provide an overview on the challenges of patterning technology for single patterning, double patterning (DP), triple patterning (TP), self-aligned double patterning and EUV patterning, based on the learning of BEOL (Back End of Line) patterning technology development. We will focus on BEOL patterning technology challenges for 14nm high volume manufacturing, and demonstrate the patterning solutions for DP and TP 1D and 2D structure optimization. We will elaborate on process enhancements and controls such as CD, tip-to-tip and iso-dense loading optimization, the integrated patterning solution for open and short yield improvement and via-to-metal reliability improvement, the multi-variant APC control for process stability improvement by APC thread reduction and thread sharing among a variety of products. The success of BEOL patterning technology is dependent on patterning capability, process robustness and cost of patterning solutions.

4:20pm **PS+EM-WeA7 Innovative Approaches for Future Challenges in MOL/BEOL Etch*, Ryukichi Shimizu,*** Tokyo Electron Miyagi Limited, Japan **INVITED**

Critical dimensions (CD) continue to shrink driven by the quest for cheaper, faster and less power-consuming devices. If simple shrink was not enough, all of the back end, middle and front end of line (BEOL, MOL and MOL) also have introduced structural complexity and stringent topographic dimension, material property integrity and fundamental integration yield requirements. Self-aligned contact (SAC), high aspect ratio contact (HARC) and damascene structures in the MOL and BEOL typify challenging integrations. SAC structures are formed by oxide being etched from a nitride encasement. The oxide must be etched both beside and over thin (few nm) nitride films with near infinite selectivity as horizontal nitride layers can be exposed far before the deepest oxide in contact vias are removed. These structures are subject to “plugging” if the films get to thick, loss of nitride if the films get too thin, and etch rate or profile integrity loss elsewhere due to imbalances in ion energy flux or radical loss due to shadowing in a deep via. Obtaining the perfect balance of radical flux, ion flux and ion energy for these structures over a single die, let alone an entire wafer full of dies, is nearly impossible. Put in more general terms, fabrication challenges for plasma etch related to controlling local CD Uniformity (LCDU) and mitigating depth loading and CD loading are ever present due to difference in aspect ratio dependence (ARD) of transport of radicals and ions (and their energy) in features.

Atomic layer etching (ALE) has gained favor as an approach to extract more control over the fabrication of small CD complex topographic structures. The idea is that alternating steps of self-limiting processes (e.g., passivation layer formation) and desorption (e.g., the removal of a passivation layer) mitigate aspect ratio dependence effects that lead to the aforementioned problems. The problem is that not all passivation processes are self-limiting. Fluorocarbon based processes are not self-limiting rendering them quasi-atomic layer etch. Without special consideration, quasi-ALE has the same problems that continuous processes possess.

We have demonstrated the use of a new method of rapid advanced cyclic etch (RACE) comprising an isotropic CD trim step, mixed mode CVD, ALD and anisotropic bombardment to perform aspect ratio independent deposition and thereby eliminate CD bias effects. We show that X-Y CD control by ALD, CVD and trim can also be influenced by line-of-sight re-deposition from feature bottom. The ability to manage CD will be discussed as a means of enabling advanced patterning processes for both logic, interconnect and memory at advanced technology node.

5:00pm **PS+EM-WeA9 Gas-phase Pore Stuffing for Low-damage Patterning of Organo-silicate Glass Dielectric Materials*, Jean-Francois de Marneffe,*** IMEC, Belgium*; M. Fujikama, T. Yamaguchi, S. Nozawa, R. Niino, N. Sato,* Tokyo Electron Technology Solutions Limited*; R. Chanson, K. Babaei Gavan,* IMEC, Belgium*; A. Rezvanov,* IMEC, Belgium/Moscow Institute of Physics and Technology*; F. Lazzarino, Z. Tokei,* IMEC, Belgium

Capacitance gain remains of high value for lowering the interconnect RC delay in CMOS transistors, especially in the current design-technology co-optimization (DTCO) era where circuit density is maximized. In view of their superior mechanical properties, intermediate low-k dielectrics (sub-nanometer pore diameter, open porosity < 20%, k-value > 2.5) do attract nowadays most interest. CVD porous organo-silicate glasses are the most industry-relevant materials. They do suffer from processing damage, due to their porous and bi-component nature. As a consequence, some tailored protection strategies need to be developed. The gas-phase pore stuffing (GPPS) is a CVD method using two organic reactive precursors. Vaporized monomers (Gases A and B) are injected into the reactive chamber, supplied to the substrates and polymerized. Polymers are formed in the pores, deep in the bulk dielectrics, and can be removed by thermal annealing in controlled atmosphere. The GPPS technique is demonstrated on multiple OSG materials (various porosity), then applied to an OSG dielectric with nominal k-value 2.55, porosity ~ 16% and pore diameter ~ 0.8nm, which is embedded into a M1/V0 45nm ½ pitch vehicle. The target patterning sequence aims at creating a dual damascene structure by the fully self-aligned via approach (FSAV). The benefits of the GPPS is studied on the various plasma steps used in the FSAV patterning, allowing to reduce plasma damage up to 50% for the most damaging part of the FSAV patterning sequence (CO_2 ash, used for post-via strip, GPPS recess and GPPS unstuffing). The ability of the GPPS to form a protective plug is demonstrated, by excess polymerization in the pre-patterned via. By taking advantage of the specific properties of the GPPS approach, modifications of the FSAV patterning sequence are proposed, leading to potentially large capacitance gain. Various unsealing, unplugging and unstuffing options will be described, aiming at preparing the low-k surface for GPPS stuffing, and/or restoring the original porosity without residues, at the end of the patterning sequence. The gain in low-k dielectric properties, using the GPPS technique, is studied by k-value extraction on the various used vehicles.

Dr R. Chanson has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 708106.

5:20pm **PS+EM-WeA10 ALD-Sequential Etch to Address Advanced BEOL Etch/Integration Challenges*, Xinghua Sun,*** *Y.-T. Lu, K. Lutker-Lee, A. Raley,* TEL Technology Center, America, LLC*; D. O’Meara,* Tokyo Electctron, America, Inc.*; T. Yamamura,* Tokyo Electron Miyagi Limited*; Y. Kikuchi,* TEL Technology Center, America, LLC

As semiconductor nodes continue to scale past 7nm and beyond, control of critical dimension (CD), reactive ion etch (RIE) lag, low-k damage, material selectivity and chamfer profile becomes increasingly challenging for patterning of low-k materials in back end of line (BEOL) dual damascene processes. While modulation of plasma processing can address some of these challenges, process knobs that benefit one parameter can come into conflict with another, thereby leading to a necessity to compromise between them.

Recently, the introduction of anisotropic sequential etch, in which cyclical alternation of separated deposition and activation (etching) steps are used to decouple and control plasma chemistry, has revealed additional flexibility in profile control. However, anisotropic sequential etch tends to benefit processes that require significant boosts in etch selectivity and a controlled directional etch rate, while showing little improvement for processes where material damage is also a major concern, as in the case of low-k. As such, alternative methods to protect the low-k sidewall/corner during dual damascene processing are necessary. Introduction of a conformal, sacrificial side wall/corner protective layer through atomic layer deposition (ALD) can potentially fill this gap. Addition of an ALD-sequential etch process allows for a wide range of deposition choices, in contrast to the limited options generated through the gas chemistries typical for plasma etch. In this talk, we show how an ALD-sequential etchcan address dielectric etch challenges.

5:40pm **PS+EM-WeA11 The Underlying Role of Mechanical Rigidity and Topological Constraints in Reactive Ion Etching of Amorphous Materials*, Gyanendra Bhattarai,*** *S. Dhungana, B.J. Nordell, A.N. Caruso, M.M. Paquette,* University of Missouri-Kansas City*; W. Lanford,* University at Albany*; S.W. King,* Intel Corporation

In order for self-aligned multi-pattern techniques to be extended deep into the single digit nanometer range, new fab friendly material combinations with near perfect etch selectivity will need to be identified. This in turn requires a greater understanding of the interplay between plasma etching processes and the properties of the material being etched. While some qualitative correlations between dry etch rates and material properties such as composition, porosity, and density have been reported, more quantitative relationships have been generally lacking. In this regard, we demonstrate that analytical expressions derived to describe the material dependence of the yield for ion-induced sputter processes can be extended to reactive ion etch processes. Specifically, we first demonstrate a direct relationship between the atomic surface binding energy (U_{sb},), bulk modulus, and ion sputter yield for the elements, and then subsequently prove our hypothesis for amorphous multi-element compounds by demonstrating that the same relationships exist between the reactive ion etch (RIE) rate and nanoindentation Young’s modulus for a series of a-SiN_x:H and a-SiO_xC_y:H thin films. The impact of a materials network topology is further revealed via application of the Phillips–Thorpe theory of topological constraints, which directly relates Young’s modulus to the mean atomic coordination ($<r>$) for an amorphous solid. The combined analysis allows the observed trends and plateaus in the RIE rate versus modulus to be ultimately reinterpreted in terms of the atomic structure of the target material through consideration of $<r>$. These findings establish the important underlying role of mechanical rigidity and network topology in ion–solid interactions and provide a new consideration for the design and optimization materials for self-aligned pitch division / multi-pattern technologies.

6:00pm **PS+EM-WeA12 Plasma Processing of Phase Change Materials for PCRAM***, N.D. Altieri,* ***Ernest Chen****, J.P. Chang,* University of California, Los Angeles*; S.W. Fong, C.M. Neumann, H.-S. Wong,* Stanford University*; M. Shen, T.B. Lill,* Lam Research Corporation

The manipulation of the amorphous to crystalline phase transition observed in chalcogenide glasses for non-volatile memory applications has been studied for many years since its initial conception. However, only recently has innovation in both materials development and memory device architecture enabled phase change random access memory (PCRAM) to become a promising candidate for applications such as neuromorphic computing.

Understanding the effects of plasma processing as well as post-processing damage of the phase change material (PCM) utilized in PCRAM is crucial to ensuring proper device performance. The studies presented herein focus on the behavior of $Ge_2Sb_2Te_5$ (GST-225) in conjunction with H_2 and CH_4 discharges as well as the roles of O_2 and N_2 through the use of a custom-built integrated ion beam chamber, inductively coupled plasma reactor, and *in-situ* x-ray photoelectron and quadrupole mass spectrometers.

Etch and gas phase reaction byproducts for single element Ge, Sb, and Te as well as GST-225 in hydrogen and methane have been identified through the use of quadrupole mass spectrometry and optical emission spectroscopy. X-ray photoelectron spectroscopy has been used to characterize surface bonding states and film composition across a wide parameter space, including low and high pressures as well as varying feed gas compositions.

Methane and hydrogen-based discharges were identified as capable GST etchant chemistries, resulting in rates up to 80 nm/min; however, the post-processing film composition was found to be strongly dependent on the chosen etch chemistry. Hydrogen radicals were identified as the dominant etchant species and resulted in the preferential removal of Sb and Te at low (15 mTorr) and high (75 mTorr) pressure conditions through the formation of volatile hydride products. Post-processing surface analysis indicated a substantial decrease in Sb and Te concentration from their initial 22 and 55 atomic percent to 3 and 4 atomic percent as well as an accumulation of Ge on the post-etch surface. Tuning of the etch chemistry was further explored through the use of auxiliary N_2 in order to modify the etch rate and preserve the starting 2:2:5 stoichiometry crucial to proper PCRAM device performance.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 202A - Session SA+AS+MI-WeA

Hard X-Ray Photoemission for Probing Buried Interfaces

Moderators: Zahid Hussain, Advanced Light Source, Lawrence Berkeley National Laboratory, Olivier Renault, CEA-LETI, France

2:20pm **SA+AS+MI-WeA1 Element-resolved Electronic Band Structure of Ga(Mn)As Measured by Standing-wave Hard X-ray Angle-resolved Photoemission***,* ***Slavomir Nemsak****,* Advanced Light Source, Lawrence Berkeley National Laboratory*; M. Gehlmann, C.-T. Kuo,* University of California, Davis*; T.-L. Lee,* Diamond Light Source Diamond House, Harwell Science and Innovation Campus*; L. Plucinski,* Forschungszentrum Juelich GmbH, Germany*; J. Minar,* University of West Bohemia*; C.M. Schneider,* Forschungszentrum Juelich GmbH, Germany*; C.S. Fadley,* University of California, Davis

Electronic band structure of the dilute magnetic semiconductor Ga$_{(1-x)}$Mn$_x$As was obtained using hard X-ray angle-resolved photoemission. The element- and site-sensitivity of the measurements was achieved by forming a strong X-ray standing-wave generated by Bragg reflection from the (111) atomic planes of both undoped GaAs and Mn-doped thin films. Due to the uneven occupancy of (111) planes by either Ga(Mn) or As atoms, the element-specific band structure can be obtained with a help of the SW modulation in core levels. Measured momentum- and element-resolved bulk electronic structure was compared to element-projected Bloch spectral functions with excellent agreement between experiment and theory. Apart from the site specific decomposition of the electronic structure, the SW measurements also confirmed a substitutional presence of Mn atoms at the Ga sites. This novel technique should be applicable to a broad range of complex materials.

2:40pm **SA+AS+MI-WeA2 Probing Surface Band Bending of Polar GaN by Hard X-ray Photoemission Combined with X-ray Total Reflection***,* ***Shigenori Ueda****,* NIMS, Japan

GaN is known as a polar semiconductor due to an alternative stacking of Ga and N layers along the c-axis. Ohsawa *et al*. [1] showed the difference in valence band spectral shapes of the bulk Ga- and N-polar GaN single crystals by using polarization dependent hard X-ray photoemission spectroscopy (HAXPES). In general, HAXPES is a bulk-sensitive probe [2], and take-off angle (TOA) dependent of photoelectron gives depth information [3]. However, the decrease of the photoemission intensity occurs in lower TOA, and the valence band spectra depend on TOA [3] due to the matrix element effect [4].

In this work, HAXPES combined with X-ray total reflection was used to obtain a depth-resolved electronic structure instead of TOA dependent measurements. The change of incidence angle within 1 degree around the critical angle of X-ray total reflection drastically changes the attenuation length of X-ray in solids.

We have measured the core-level and valence band HAXPES spectra of commercially available bulk single crystalline GaN for Ga and N polar faces in the case of inelastic mean free path of 2.17, 3.73, and 7.69 nm. Undoped *n*-type GaN crystal with fine polished surfaces was used. For the Ga-polar face, large band bending behavior was observed, while the band bending was small for the N-polar face. The Ga 3s and N 1s core-level spectra also showed the polarity dependent band bending behavior. We found that GaN near the surface is degraded in both the polar faces. This result suggests that high quality single crystalline GaN with fine surface treatment is required for detecting the intrinsic electronic structure of GaN. Finally we note that HAXPES combined with X-ray total reflection is useful method for depth-resolved electronic structure measurements, since the data acquisition time in this method is 10 or more faster than that in TOA dependent measurement, and the matrix element effect is almost negligible in this method.

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3:00pm **SA+AS+MI-WeA3 Interfaces in Cycled Battery Electrodes: Insights from HAXPES Studies***,* ***Julia Maibach****,* Karlruhe Institut of Technology (KIT), Germany **INVITED**

Rechargeable ion batteries such as lithium and sodium ion batteries generally consist of a negative electrode, a positive electrode and an ion conducting electrolyte. The contacts between the different materials are key to the electrochemical energy storage process and at the surfaces of the electrodes and at the interfaces to the electrolyte, reactions crucial to long-term, safe battery operation take place. Due to its surface and chemical sensitivity, photoelectron spectroscopy has therefore become a widely used tool to characterize and understand the processes and phenomena in these electrochemical energy storage systems.

Looking in more detail, a battery electrode itself is a complex system as it consists of many different components such as the active storage material, conductive additives as well as binders to keep the particles attached to a metal foil, which acts as a current collector. This complexity of mixed materials and morphologies further increases when the electrodes are cycled electrochemically due to the desired storage processes and due to reactions with the battery electrolyte leading to interface layer formation.

These highly complex systems of cycled battery electrodes bring new challenges when studied with photoelectron spectroscopy. In this presentation, observed peak shifts for cycled battery electrodes will be discussed in depth. Particular emphasis will be given to the buried interfaces. Here, hard x-ray photoelectron spectroscopy (HAXPES) is one of the few available techniques that can access the buried interface while maintaining the chemical information from the delicate battery interface layers. Based on HAXPES experiments, the role of the buried interfaces and their importance in both battery operation as well as in photoelectron spectroscopy characterization of cycled electrodes will be discussed.

Additionally, spectral changes due to electrode potentials as well as lithiation effects will be discussed. These strongly depend on the nature of the active material and therefore need to be considered carefully to achieve consistent data interpretation. Combining all presented effects, a strategy for photoelectron spectroscopy experiments on cycled battery electrodes will be proposed that takes buried interfaces into account.

4:20pm **SA+AS+MI-WeA7 Development of Ambient Pressure HAXPES and other HAXPES Measurements at SPring-8 for Buried Interface*, Yasumasa Takagi,*** Japan Synchrotron Radiation Research Institute (JASRI), Japan **INVITED**

A near ambient pressure photoelectron spectroscopy measurement that use with hard X-rays (AP-HAXPES) were conducted at the BL36XU of SPring-8. The AP-HAXPES system with a commercial differential pumping-type spectrometer (R4000 HiPP-2, Scienta Omicron Inc.) was installed in the beamline. The excitation light of 7.94 keV focused to a beam size of 20 µm x 20 µm on the sample surface was used. The standard aperture size at the top of the front cone in the spectrometer is a diameter of 300 µm. In this report, we replaced the front cone with our home-made one with an aperture diameter of 30 µm to increase the pressure limit in the AP-HAXPES measurement. Meanwhile, we have adapted the working distance of 60 µm in order not to perturb the gas environment at the sample surface.

We measured the XPS spectra of the Au(111) surface grown on a mica substrate under various gas pressures using the AP-HAXPES equipment. The intensity decay of the Au 4f spectra with an increasing gas pressure from 1 Pa to 100 kPa. Here we use "100 kPa" as the atmospheric pressure. The XPS measurement was not affected by the ambient gas at a pressure of 1 Pa. As the gas pressure increased, the signal intensity decreased because the photoelectrons were scattered by the ambient gas while passing through the sample to the detector. Although the signal intensity was very weak at the atmospheric pressure, the peaks of $4f_{5/2}$ and $4f_{7/2}$ can be detected. The signal-to-noise ratio can be improved by a prolonged acquisition time. The $4f_{7/2}$ and $4f_{5/2}$ peaks are clearly found in the spectrum at the atmospheric pressure in an acquisition time of 30 min. The Shirley background was subtracted from the spectrum, and the plots were fitted with a Voigt function. The curve fitting result shows that the energy difference between the $4f_{7/2}$ and $4f_{5/2}$ peaks is 3.7 eV and the intensity ratio $4f_{7/2}$:$4f_{5/2}$ is almost 4:3. These values are in good agreement with the standard value of the Au 4f peaks. Thus, a photoelectron spectroscopy under atmospheric pressure was successfully obtained using an aperture of 30 µm.

5:00pm **SA+AS+MI-WeA9 Operando HAXPES Investigations of La Manganite-based Resistive Memories*, Eugénie Martinez,*** CEA/LETI-University Grenoble Alpes, France*; BM. Meunier,* Univ. Grenoble Alpes, CEA, LETI & LMGP, CNRS, France*; DP. Pla,* Univ. Grenoble Alpes, LMGP, CNRS, France*; RRL. Rodriguez-Lamas,* Univ. Grenoble Alpes, LMGP, CNRS France*; MB. Burriel, CJ. Jimenez,* Univ. Grenoble Alpes, LMGP, CNRS, France*; JPR. Rueff,* Synchrotron SOLEIL, France*; Y. Yamashita, S. Ueda,* NIMS, Japan*; O.J. Renault,* CEA/LETI-University Grenoble Alpes, France

The use of perovskite oxides in resistive random access memories (RRAMs) is considered for the next generation of non-volatile memories (NVMs) [1]. Indeed, their highly tunable ionic and electronic transport properties open new possibilities for multilevel storage capacity. In particular, manganese oxides, such as $LaMnO_{3+d}$ (LMO), are among the most promising candidates [2].The switching mechanism is related to oxygen transport, yielding to the creation and annihilation of oxygen vacancies through the functional layer. However, two main mechanisms based on filaments or 2D interfacial effects must be discriminated to better understand and control the devices properties.

We investigate here the key role of oxygen in the switching mechanism of LMO-based RRAMs using hard X-ray photoelectron spectroscopy (HAXPES). This technique allows learning about electrochemical reactions involved in the structure with sufficient depth sensitivity. Operando HAXPES was performed at Soleil and SPring-8 to investigate in-situ resistive switching. Measurements were done while biasing the memory with opposite polarities, to reach successively low and high resistance states. In particular, a chemical analysis of the interface between the active electrode and the LMO was done after *Set* and *Reset* operations.

Results show modifications of the oxygen core level spectra. The peak assigned to interfacial LMO shifts as a function of bias voltage, contrary to the bulk LMO component. These results highlight variations in charges concentration at the electrode/LMO interface, as a result of creation/annihilation of interfacial defects, such as oxygen vacancies. Complementary trends regarding La3*d* and Mn3*s*/2*p* spectra will be discussed in terms of oxidation and reduction phenomena, related to variations of the oxygen content at the electrode/LMO interface.

[1] Jin YL, Jin KJ, Ge C, Lu HB, Yang GZ, Resistive switching phenomena in complex oxide heterostructures, Modern Physics Letters B, 2013;27(29)1330021.

[2] Pan F, Gao S, Chen C, Song C, Zeng F, Recent progress in resistive random access memories: Materials, switching mechanisms and performance, Mater. Sci. Eng. R 2014,83:1-59.

5:20pm **SA+AS+MI-WeA10 Combining Hard and Soft X-ray Angle-resolved Photoemission to Probe the Bulk Electronic Structure of Engineered Quantum Solids*, Alexander Gray,*** Temple University **INVITED**

Angle-resolved photoelectron spectroscopy, or ARPES, is a powerful and well-established experimental technique for probing the momentum-resolved electronic structure of matter. In this talk, I will discuss several promising new directions in this field, which stem from experimental and theoretical studies wherein angle-resolved photoemission is carried out at higher excitation energies, namely in the soft and hard x-ray regimes. I will focus specifically on the recent studies of novel engineered quantum materials and heterostructures, which aim at gaining a clear understanding of the depth-dependent nanoscale evolution of materials' electronic properties at the surface, in the bulk, and across the buried interfaces by using multiple modalities of hard and soft x-ray angle-resolved photoemission both separately and in tandem with each other.

6:00pm **SA+AS+MI-WeA12 Surface/Interface Coupling in Buried Oxide Interfaces*, Conan Weiland,*** National Institute of Standards and Technology (NIST)*; A.K. Rumaiz,* Brookhaven National Laboratory*; G.E. Sterbinsky,* Argonne National Laboratory*; J.C. Woicik,* National Institute of Standards and Technology (NIST)

Oxide interfaces can host a variety of properties not found in the bulk materials. The interface between LaAlO3 (LAO) and SrTiO3 (STO) is a prototypical example; the interface of these two insulators can show conductivity, ferromagnetism, and even superconductivity. The source of these interface properties is still a matter of debate, with potential explanations including electronic reconstruction due to the polar discontinuity at the interface, chemical intermixing, and oxygen vacancies at either the interface or LAO surface. Hard x-ray photoelectron spectroscopy (HAXPES) is an excellent tool to probe these interfaces due to the enhanced and tunable probe depth afforded by a synchrotron source. We have used a combination of variable kinetic energy HAXPES and ambient pressure soft x-ray photoelectron spectroscopy (AP-XPS) to investigate the interplay between LAO film and surface structure and the LAO/STO interface. We find Al surface enrichment for most LAO films, while AP-XPS shows significant band shifts in the presence of water vapor. The role of these LAO surface features on the LAO/STO interface conductivity will be discussed.

Surface Science Division
Room 203C - Session SS+AS+EM-WeA
Semiconducting Surfaces

Moderators: Melissa Hines, Cornell University, Ludo Juurlink, Leiden University

2:20pm **SS+AS+EM-WeA1 Functionalizing Semiconductor Surfaces and Interfaces*, Stacey Bent,*** Stanford University **INVITED**

Semiconductor surface and interface science serves as the foundation for applications ranging from microelectronics to optoelectronics to bio-sensing. Given the importance of semiconductor surface chemistry in important technologies of today, understanding the fundamental chemistry at a molecular level is key to future advances. This talk will describe studies on the adsorption of organic molecules at semiconductor surfaces, aimed at the ultimate goal of controlling the chemical and electrical properties of these hybrid systems. The presentation will examine model systems of molecular adsorption on the Ge(100)-2×1 surface using a combination of experimental and theoretical methods. The reactivity of different functional groups will be described, with particular focus on reactions of bi- and trifunctional molecules. The results help elucidate the way in which the molecular structure as well as the identity of the reactive moieties affect the product distribution of the molecules upon adsorption. Monolayer surface chemistry is also extended to the formation of covalently-bound organic multilayers through the process of molecular layer deposition (MLD). Results will be presented of our studies to understand MLD mechanisms and bonding. We show that chain termination events during MLD can be counteracted by absorption of precursors into the MLD film, which reintroduces reactive sites that lead to continuation of film growth. We will also describe new MLD chemistries, including photo-initiated MLD that forms new carbon-carbon bonds at the surface.

3:00pm **SS+AS+EM-WeA3 Atomic Structure of UHV-prepared GaP(111)A Surface and its Reactivity Towards Simple Molecules***, **Denis Potapenko**, X. Yang, B.E. Koel,* Princeton University

Effective pyridine-catalyzed photo-reduction of CO_2 to methanol has been demonstrated on p-type GaP(111)A photocathode. Despite the considerable effort there is still no consensus about either the molecular mechanisms of this process or the role of electrode's surface. As a part of larger effort aimed at elucidation of the mechanisms of CO_2 photoreduction we have conducted a UHV study of the atomic-scale structure and reactivity of the single-crystal GaP(111)A surface. Atomic-resolution STM images supported by LEED data show that ion sputtered and annealed surface exhibit both 2 x 2 Ga-vacancy reconstruction and relatively disordered P-trimer formations. The stoichiometric excess of Ga leads to formation of large droplets on the surface. TPD experiments and IR spectroscopy with water and methanol demonstrate dissociative adsorption of these molecules that leads to recombinative desorption around 300 K.

3:20pm **SS+AS+EM-WeA4 Stabilization Mechanism of the Se- or S-treated GaAs(111)B Surface***, **Shunji Goto**,* The University of Electro-Communications (UEC-Tokyo), Japan*; A. Ohtake,* National Institute for Materials Science (NIMS), Japan*; J.N. Nakamura,* The University of Electro-Communications (UEC-Tokyo), Japan

GaAs surfaces are stabilized by surface treatments with S or Se because of the reduction of the dangling bond density [1,2]. Recently, it has been reported that when the GaAs(111)B-(2 x 2) As trimer surface is treated with Se, the diffraction pattern changes from (2 x 2) to (1 x 1) [3]. The Se-treated GaAs(111)B-(1 x 1) surface was considered to have a simple structure; all As atoms of the ideal (111)B surface are replaced by Se atoms. However, a scanning tunneling microscope (STM) image shows highly disordered array of bright features with a density of 0.25 per (2 x 2) unit [4,5]. This is incompatible with the simple structure model for (1 x 1). Very recently, another structure model has been proposed for the Se-treated surface, where three As atoms on the topmost surface are replaced by Se atoms per (2 x 2) unit. This As / Se terminated model is electronically stable because the so-called electron counting rule is satisfied and the STM simulations for this model reproduces the most of features of STM experiments. In this study, we discuss the structural stability of the As / Se termination model from the viewpoint of the formation energy. We depict a phase diagram as functions of chemical potentials of Se (μ(Se)) and As (μ(As)) using the first-principles calculations within the density functional theory.

Under the As-rich and Se-poor conditions, the (2 x 2) As-trimer surface is the most stable phase. The As / Se terminated surface appears in the phase diagram under more As (Se) poor (rich) conditions, being consistent with the recent experiment [5]. It is noted that the fully-Se-terminated (1 x 1) surface can exist as a stable phase in the limit of Se-rich condition, whereas this surface does not satisfy the electron counting rule and has a metallic surface state attributed to surplus electrons of Se. At the fully-Se-terminated surface, a lone pair forms at each Se site and resultant excess electrons occupy the anti-bonding orbital of the outermost bilayer. As a result, the surface Se atoms hardly leave any dangling bond. We have also found that the S-treated surface is passivated by a similar mechanism.

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[2] V. N. Bessolov and M. V. Lebedev, Fiz. Tekh. Poluprovodn **46**, 10201 (1998).

[3] D. A. Woolf, Z. Sobiesierski, D. I. Westwood, and R. H. Williams, J. Appl. Phys. **71**, 4908 (1992)

[4] A. Ohtake and Y. Sakuma, Cryst. Growth Des. **17**, 363 (2017).

[5] A. Ohtake, S. Goto, and J. Nakamura, Sci. Rep., **8**, 1220 (2018).

4:20pm **SS+AS+EM-WeA7 Novel Pathways in Reaching Buried Interfaces of Organic/Inorganic Hybrid Systems: A Mechanistic Understanding of Polymer Adsorption on Passivated Metal Oxide Surfaces***, **Tom Hauffman**, S. Pletincx, K. Marcoen, F. Cavezza,* Vrije Universiteit Brussel, Belgium*; L.-L. Fockaert, J.M.C. Mol,* Technical University Delft, Netherlands*; H. Terryn,* Vrije Universiteit Brussel, Belgium

The interface between a metal oxide and its coating is of great importance for the durability and efficiency of the entire organic/inorganic hybrid system. However, the analysis of such solid/solid interfaces is challenging, as they are masked by a µm-thick polymer layer on one side and a thick metal oxide matrix on the other side. The main difficulty will be to investigate buried interfaces non-destructively with conventional surface analysis techniques.[1,2]

In this work, we characterize interfacial interactions of several ultrathin polymeric films with aluminum and zinc oxides by utilizing novel methodologies, leading to the characterization of a realistic model interface. The adsorption mechanisms are established by using XPS for chemical state information and ToF-SIMS for direct molecular information of these ultrathin organic overlayers.

The use of these nanometer thin films opens up the possibility of an in situ characterization of environmental influences such as water ingress. The use of Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) is employed to describe the adsorption mechanism in the presence of water vapor. Furthermore, ATR-FTIR Kretschmann is utilized to obtain a near-interface infrared spectrum while simultaneously, the influence of an above-the-polymer electrolyte (such as water) on the interface is characterized.[3]

The homogeneity of these interfacial interactions is characterized on the nanoscale using nano-infrared spectroscopy. This novel technique allows to conduct infrared spectroscopy on the nanoscale by using an AFM tip, which probes the expansion of the material due to IR absorbance. This results in a local vibrational spectrum.

This work comprises novel synthesis routes and methodologies, which enable to probe interfacial changes in hybrid systems non-destructively and in situ. As such, coatings systems can be optimized with respect to the bare substrate.

(1) van den Brand, J.; Blajiev, O.; Beentjes, P. C. J.; Terryn, H.; de Wit, J. H. W. Interaction of Anhydride and Carboxylic Acid Compounds with Aluminum Oxide Surfaces Studied Using Infrared Reflection Absorption Spectroscopy. *Langmuir***2004**,*20*(15), 6308–6317.

(2) Hinder, S. J.; Lowe, C.; Maxted, J. T.; Watts, J. F. A ToF-SIMS Investigation of a Buried Polymer/polymer Interface Exposed by Ultra-Low-Angle Microtomy. *Surf. Interface Anal.***2004**, *36*(12), 1575–1581.

(3) Pletincx, S.; Trotochaud, L.; Fockaert, L.-L.; Mol, J. M. C.; Head, A.; Karslıoğlu, O.; Bluhm, H.; Terryn, H.; Hauffman, T. In Situ Characterization of the Initial Effect of Water on Molecular Interactions at the Interface of Organic/Inorganic Hybrid Systems. *Sci. Rep.***2017**, *7*(45123).

4:40pm **SS+AS+EM-WeA8 Surface Modification of Metal Oxide Surfaces with Gas-Phase Propiolic Acid for Dye Sensitization by Click Reaction***, **Chuan He**, A.V. Teplyakov, B. Abraham, M. Konh, Z. Li, L. Gundlach, S. Bai,* University of Delaware*; E. Galoppini, H. Fan, R. Harmer,* Rutgers, the State University of New Jersey

The dye sensitization on metal oxide (ZnO, TiO_2, Fe_2O_3, CuO) surfaces has attracted plenteous attention due to their numerous applications in solar energy conversion, photo-catalysis, sensing, etc. Substantial research efforts focused on designing different dyes and surface nanostructuring. However, the actual chemical attachment schemes still heavily rely on the use of sensitizer molecules functionalized with carboxylic (COOH) or phosphonic ($P(O)(OH)_2$) anchor groups. Despite consequential progress in chemical modification schemes, the very nature of these functional groups may cause very pronounced surface morphology change of the nanomaterials designed because of etching process in liquid phase. In addition, these acidic groups often lead to the formation of multiple binding configurations (such as monodentate or bidentate miixtures) on the surface. To address both issues, we developed a two-step preparation procedure to achieve the morphology preservation of metal oxide surfaces and well-defined covalent binding of the intersurface functionality. The first step requires exposing clean metal oxide nanostructures to a gas-phase prop-2-ynoic acid (propiolic acid) in medium or high vacuum, which results in the formation of a robust and stable surface-bound carboxylate with ethynyl groups available for further modification. For the second step, we applied copper catalyzed click reaction on this preserved surface to covalently bind dye molecules functionalized with azido groups to these pre-functionalized surfaces. For example, a suitable organic dye (9-(4-azidophenyl)-2,5-di-tert-butylperylene (DTBPe-Ph-N_3)) was used to investigate a distinct signature of covalently-bound dye molecules on ZnO nanorods surface. In this study, we have confirmed the morphology preservation and selective covalent attachment of the carboxylic acid onto the metal oxide surface by the combination of measurements including scanning electron microscopy (SEM), infrared, X-ray absorption photoelectron spectroscopy (XPS), solid-state 13C NMR, transient absorption spectroscopy (TA) and density functional theory (DFT) calculations.

5:00pm **SS+AS+EM-WeA9 Solar Energy Storage in the Norbornadiene-quadricyclane System: From Surface Science to In-situ Photochemistry and photospectroelectrochemistry**, *M. Schwarz, F. Waidhas, C. Schuschke,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; S. Mohr,* Friedrich-Alexander-Universität Erlangen-Nürnberg*; O. Brummel, T. Döpper, C. Weiss, K. Civale,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; M. Jevric,* Chalmers University of Technology, Gothenburg, Sweden*; J. Bachmann,* Friedrich-Alexander-Universität Erlangen-Nürnberg. Germany*; A. Görling, A. Hirsch,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; K. Moth-Poulsen,* Chalmers University of Technology, Gothenburg, Sweden*; **Jörg Libuda**,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Photochemical isomerization of small organic molecules enables chemical energy storage via a single-photon-single-molecule process. A prototypical example is the conversion of norbornadiene (NBD) to its strained metastable valence isomer quadricyclane (QC), which releases up to 100 kJ/mol upon cycloreversion. This makes the NBD-QC system a solar fuel with an energy density comparable to state-of-the-art batteries.

In order to obtain a better understanding of NBD-based energy storage systems, we studied both the photochemical conversion and the catalytically and electrochemically triggered back-conversion at atomically defined interfaces. We combined vibrational spectroscopy with in-situ photochemistry in ultrahigh vacuum (UHV) and in electrochemical (EC) environments. In UHV, NBD and QC films were grown by physical vapor deposition (PVD) on Pt(111). By infrared refection absorption spectroscopy (IRAS), we observe spontaneous cycloreversion in QC monolayers even at 130 K, while QC multilayers are stable. Adsorbed NBD adopts a η_2:η_1 geometry which involves an agostic C-H-Pt interaction. At 300 K, this species undergoes dehydrogenation by splitting off the agostic H.

In UHV environments, the conversion from NBD to QC can be triggered in-situ by UV light and a co-deposited photosensitizer (PS). In electrochemical environments, back-conversion can be triggered by the electrode. On Pt(111) electrodes, we monitored the back-conversion in-situ by electrochemical infrared reflection absorption spectroscopy (EC-IRRAS). The corresponding spectra were analyzed based on simulated spectra from density functional theory (DFT). Using a new photoelectrochemical IRRAS setup (PEC-IRRAS), we monitored the complete storage and release cycle by in-situ vibrational spectroscopy. Selectivities were determined both for the conversion and the back-conversion, showing that the stability of the PS is a critical step in the storage cycle. Much higher reversibility could be obtained using new NBD derivatives which avoid an additional PS.

To better control the energy transfer via the electrode interface, we investigated NBD derivatives anchored via a carboxylic-acid function to atomically defined oxide surfaces. In UHV, dense monolayers of surface-anchored NBD derivatives were prepared by PVD onto $Co_3O_4(111)$ films on Ir(100). The molecules adopt an upright-standing orientation with the NBD units pointing away from the interface. Finally, we explored the behavior of these films in (photo)electrochemical environments.

[1] O. Brummel et al., ChemSusChem 9, 1424 (2016).

[2] U. Bauer at al., Chem. Eur. J. 23, 1613 (2017).

[3] O. Brummel et al., J. Phys. Chem. Lett., 8, 2819 (2017).

5:20pm **SS+AS+EM-WeA10 In-situ Characterization of Photon induced Chemistries in Organotin Clusters with Ambient Pressure XPS**, ***J. Trey Diulus***[1]*, R.T. Frederick,* Oregon State University*; M. Li,* Rutgers, the State University of New Jersey*; D.C. Hutchison, I. Lyubinetsky, L. Árnadóttir, M.R. Olsen,* Oregon State University*; E.L. Garfunkel,* Rutgers, the State University of New Jersey*; M. Nyman,* Oregon State University*; H. Ogasawara,* SLAC National Accelerator Laboratory*; G.S. Herman,* Oregon State University

Solution-based organometallic nanoclusters are unique nanoscale material precursors due to the precise control over their size, shape, and structure. The interaction of photons with these clusters can result in the preferential removal of organic ligands at room temperature. This process leads to a change in solubility, which makes these materials prime candidates for next-generation photoresists for extreme ultraviolet (EUV) nanolithography. In this study, we are investigating the interaction of soft X-ray radiation with organotin based clusters to better understand the transition from organometallic to metal oxide nanoclusters. As a model system we are studying the charge neutral, sodium templated, butyl-tin Keggin (β-NaSn$_{13}$) cluster $[NaO_4(BuSn)_{12}(OH)_3(O)_9(OCH_3)_{12}(Sn(H_2O)_2)]$. For analysis, the β-NaSn$_{13}$ clusters were dissolved in 2-heptanone and spin-coated to form uniform thin films (~20 nm thick). Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) was used to measure the Sn 3d, O 1s, and C 1s core-levels, using photon energies above and below key absorption edges. These measurements allowed us to characterize changes in the both the atomic concentrations and chemical states of β-NaSn$_{13}$ under a range of ambient conditions, including ultrahigh vacuum and multiple partial pressures (between 0.01 to 1 Torr) of oxygen, water, methanol, nitrogen, and hydrogen. Successive C 1s scans were collected during exposure to measure the change in intensity with respect to exposure time, ambient, and photon energy. A significant reduction in the C 1s signal was observed for oxygen ambients, suggesting the oxygen partial pressure was able to increase the rate of butyl group desorption from the β-NaSn$_{13}$ clusters. Furthermore, a photon dose array was collected in each condition to determine whether ambient conditions have an effect on the photon induced chemistries leading to a solubility transition. The dose array was plotted as contrast curves, which indicate that an oxygen ambient significantly lowers the required photon dose relative to UHV. We also found that a water ambient significantly increases the required photon dose compared to an oxygen or UHV ambient. These studies ultimately improve the understanding of photon induced chemistries in the β-NaSn$_{13}$ based thin films and provide mechanistic insights for the formation of tin oxide nanomaterials at surfaces.

5:40pm **SS+AS+EM-WeA11 Integrated Photonics Driven Electron Emission from LaB$_6$ Nanoparticles***, **Fatemeh Rezaeifar**, R. Kapadia,* University of Southern California

In this report, we demonstrate the novel approach of integrated photonics waveguide driven electron emission from Lanthanum hexaboride (LaB$_6$) nanoparticles drop-casted over the surface of an optical waveguide. We use integrated waveguide under LaB$_6$ electron emitter as a mean to transport photons and evanescently couple them to emitter. This evanescent coupling occurs through longer interaction length and photons can be absorbed efficiently compared to free space laser illumination from top on a metallic emitter. Furthermore, nanoparticles with the average diameter of 4 nm are at the order of electron mean free path and electron emission occurs with fewer scattering compared to electron emission from conventional bulky metallic emitters. As such, in our proposed device, the higher optical absorption along with fewer scattering inside nanoparticles enable us with larger quantum efficiency electron emitters beyond the available photon driven emitters.

We experimentally studied the photon driven electron emission characteristics obtained by coupling of CW laser (wavelength = 405 nm) to LaB$_6$ nanoparticle emitters drop-casted on top surface of the silicon nitride (Si_3N_4) integrated waveguide with height of 5 µm and width of 50 µm. Optical V-groove was fabricated for coupling 405 nm laser from 200 µm optical fiber in to Si_3N_4 waveguide. The work function of the LaB$_6$ is only 2.69 eV and it requires very small E-field to collect the photon driven emitted electrons. We observed photocurrent at E-field as small as 0.3 V/µm while the dark current detection from LaB$_6$ nanoparticles begins at higher E-field, 3.5 V/µm. In addition, we present the photocurrent dependency on the laser power. At small E-field in which no tunneling is possible, we observed a linear relation between the photocurrent and laser power indicating single photon ability for this emission process. This matches to the expected slope of 1 for single photon absorption process, given that the work function of LaB$_6$ is only 2.69 eV, and our photon energy at 405 nm is 3.1 eV. Finally, we present the comparative results for the emission properties from LaB$_6$ nanoparticles illuminated with free space laser to evaluate the performance of the proposed integrated photonics driven emitters. While free space illuminated method results in emission current as small as 1 pA with 390 mW of laser power, the integrated photonics driven emitter emits above 50 pA with much smaller laser power transporting inside the optical waveguide, 100 µW. As such, we conclude integrated photonics driven emitter as a potential solution for increasing the quantum efficiency of the future electron emitters.

6:00pm **SS+AS+EM-WeA12 Photon Stimulated Desorption and Diffusion of CO on $TiO_2(110)$***, **Nikolay Petrik**, R. Mu, A. Dahal, Z.-T. Wang, Z. Dohnalek, I. Lyubinetsky, G.A. Kimmel,* Pacific Northwest National Laboratory

Thermal diffusion of CO adsorbed on rutile $TiO_2(110)$ was studied in the 20 - 110 K range using photon-stimulated desorption (PSD), temperature programmed desorption (TPD) and scanning tunneling microscopy. During UV irradiation, CO desorbs from certain photoactive sites (e.g. oxygen

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

vacancies). This phenomenon was exploited to study CO thermal diffusion in three steps: first empty these sites during a first irradiation cycle, then replenish them with CO during annealing, and finally probe the active site occupancy in the second PSD cycle. The PSD and TPD experiments show that the CO diffusion rate correlates with the CO adsorption energy – stronger binding corresponds to slower diffusion. Increasing the CO coverage or hydroxylation of the surface decreases the CO binding and increases the CO diffusion rate. Relative to the reduced surface, the CO adsorption energy increases and the diffusion decreases on the oxidized surface. The CO diffusion kinetics can be modeled satisfactorily as an Arrhenius process with a "normal" prefactor (i.e. $\nu = 10^{12}\ s^{-1}$) and a Gaussian distribution of activation energies where the peak of the distribution is ~0.28 eV and the full width at half maximum (FWHM) is ~0.1 eV at the lowest coverages. The observations are consistent with a significant electrostatic component of the CO binding energy on the $TiO_2(110)$ surface which is affected by changes in the surface dipole and dipole-dipole interactions.

Thin Films Division
Room 102A - Session TF+EM+MI-WeA

Thin Film Processes for Electronics and Optics II

Moderators: Hilal Cansizoglu, University of California, Davis, John F. Conley, Jr., Oregon State University

2:20pm **TF+EM+MI-WeA1 What can we Benefit from Nanochemistry of Crystalline Silicon?***, **Naoto Shirahata**,* National Institute for Materials Science, Tsukuba, Japan **INVITED**

The richly tunable optical properties of colloidal silicon nanoparticles, in conjunction with flexible functionalization of their surfaces, makes them important class of materials with various potential applications in the ranging from medicine to optoelectronics. Bulk crystal of silicon is an indirect bandgap semiconductor, resulting in poor light emission and a weak absorption onset – major technological barrier for their use in photonics. The successful approaches in transforming silicon into efficient light emitters are appearance of the quantum confinement effect and reformation in atomic structure and periodicity from diamond cubic lattice to nanoclusters having a direct gap structure. The improved optical properties including photoluminescence quantum yields, require the efficient radiation recombination between photogenerated electron-hole pairs across the gaps. To achieve this, the surface chemistry plays an important role. In particular, the formation of carbon-silicon linkage at the surface of the nanoclusters results in the enhanced radiative recombination probability.

Today's talk starts by describing a brief overview of light emitting silicon nanoparticles to understand their place in the world of colloidal semiconductor nanocrystals. Next, the talk focuses on the reliable approaches to give a fine tuning of photoluminescence spectra with high spectral symmetries and impressively narrow spectral linewidths. Recent progress of chemical synthesis and surface functionalization of silicon nanoparticles is then demonstrated, in conjunction with their applications including efficient light emitting diodes and non-toxic biomarkers adapted for two-photon excitation fluorescence cell imaging. The performance of silicon-based light emitters are influenced significantly by surface moiety.

Since the finding of porous silicon in 1990, the free-standing, strongly luminescent silicon nanoparticles have become a masterpiece of nanoscience and nanochemistry. Such thermodynamically-stable colloidal nanoparticles will continue to lead to novel concepts of medical and device applications in near future.

3:00pm **TF+EM+MI-WeA3 Low-temperature Homoepitaxial Growth of Two-dimensional Antimony Superlattices in Silicon***, **April Jewell**, M.E. Hoenk, A.G. Carver, S. Nikzad,* Jet Propulsion Laboratory

Our group has previously reported on the growth of antimony delta-doped silicon by low-temperature molecular beam epitaxy. In this presentation we will discuss the extension of our antimony delta doping capabilities to the growth of n-type superlattices (i.e. films that incorporate multiple delta layers). We will discuss details related to growth optimization, and show results from in situ monitoring by Auger electron spectroscopy and electron diffraction. We will also report on electrical characterization of our films and preliminary device measurements.

JPL's delta doping and superlattice doping (i.e., two-dimensional "2D" doping) processes have been developed primarily for use with silicon-based scientific imagers. A key performance metric for these detectors is photometric stability, a parameter that depends largely on passivation at the detector interface. Our approach uses an atomically thin (2D), highly concentrated layer of dopant atoms embedded within nanometers of the surface. This allows for dopant concentrations in the range of 10^{13}-10^{14} cm^{-2} (10^{20}-10^{21} cm^{-3}); higher than can be achieved with 3D doping techniques. Resulting quantum effects within the highly-doped 2D layers result in exceptional stability in 2D-doped devices.

N-type 2D-doping with antimony is challenging primarily because it tends to segregate to the surface. Segregation is suppressed at low temperatures; however, this may compromise epitaxial growth and lead to poor dopant incorporation and activation. Even so, it has been shown that at sufficiently slow silicon deposition rates it is possible to maintain epitaxial growth even at low temperatures for finite thicknesses. In our previous work with single n-type delta layers, we demonstrated activated dose concentrations as high as 2×10^{14} cm^{-2} and sharp dopant profiles (~35 Å FWHM). Under the current effort we have further optimized our growth processes to achieve even sharper dopant profiles and multiple delta layers. This is enabled by switching from a standard effusion cell to a valved cracker cell for antimony evaporation, which allows for high atom and carrier densities on the order of ~10^{21} cm^{-3} with peak distribution at ~10 Å FWHM.

The performance of our low-temperature 2D-doping processes has been validated by applying both p-type and n-type superlattice-doping to fully depleted photodiodes. The superlattice-doped devices show significantly higher responsivity than the equivalent ion-implanted devices. Additionally, when exposed to pulsed X-rays the superlattice-doped devices exhibit fast response and recovery times required for use in pulsed power experiments.

4:40pm **TF+EM+MI-WeA8 Epitaxial Growth and Electrical Properties of VO_2Thin Films***, **Yang Liu**, S. Niu, T. Orvis, H. Zhang, H. Wang, J. Ravichandran,* University of Southern California

We report the epitaxial growth and the electrical properties, especially the metal-to-insulator transition (MIT) of vanadium dioxide (VO_2) thin films synthesized on lanthanum strontium aluminate tantalate (LSAT) (111) substrates by a pulsed laser deposition method. X-ray diffraction study shows that the epitaxial relation between the VO_2 thin films and LSAT substrate is given as VO_2(020)||LSAT(111) and VO_2[001]||LSAT[11-2]. We observed a sharp change of four orders of magnitude in resistance at the MIT temperature of 345K. We measured distinctive Raman spectra below and above the transition point indicating a structural transition between the insulator and metallic phases, as observed in past investigations.

5:00pm **TF+EM+MI-WeA9 A Novel Technique for the Growth of Gallium Oxide Nanowires for UV Detection***, **Badriyah Alhalaili**,* UC, Davis*; R.J. Bunk, H. Mao,* UC Davis*; R. Vidu,* UC, Davis*; H. Cansizoglu,* UC Davis*; M.S. Islam,* UC, Davis

Recently, high interest in wide bandgap semiconductors for a variety of applications has grown. Due to the unique thermal, optical, and electrical properties of Ga_2O_3, the scientists attract to the assessment of Ga_2O_3 nanowires (NWs) as a valuable material in semiconductor research fields, especially for applications in harsh environments and power electronics. Compared to thin films, nanowires exhibit a higher surface-to-volume ratio, increasing their sensitivity for detection. Additionally, nanowire devices exhibit quantum effects not seen in bulk materials and allow for crystalline materials to be grown on arbitrary substrates in spite of lattice mismatch due to lattice strain relaxation at the interface. In this work, we explore a simple and inexpensive method of growing high-density gallium oxide NWs at high temperatures. The gallium oxide NWs growth mechanism can be obtained by heating and oxidizing the gallium metal into high temperatures above 900 °C. This process can be optimized for large-scale production with high-quality, dense and long-length of gallium oxide NWs. We show the results of the characterization of the materials including the optical band gap, Schottky barrier height with metal contacts, and photoconductance of β-Ga_2O_3 nanowires. The influence of density on these Ga_2O_3 nanowires will be examined in order to determine the optimum configuration for the detection of UV light.

5:20pm **TF+EM+MI-WeA10 Enhanced Efficiency in Photon-trapping Ge-on-Si Photodiodes for Optical Data Communication***, **Hilal Cansizoglu**, C. Bartolo Perez, Y. Gao, E. Ponizovskaya Devine, S. Ghandiparsi, K.G. Polat, H.H. Mamtaz, M.F. Cansizoglu,* University of California, Davis*; T. Yamada,* University of California, Santa Cruz*; A.F. ElRefaie, S.Y. Wang,* W&WSens Devices, Inc.*; M.S. Islam,* University of California, Davis

High speed, surface illuminated Ge-on-Si *pin* photodiodes with improved efficiency are fabricated and characterized. External quantum efficiency (EQE) of the Ge-on-Si *pin* diode is enhanced to >80% at 1300 nm and 73% at 1550 nm with only 2 µm thick intrinsic Ge layer, which is required to maintain high speed operation. Improved EQE is achieved by guiding incident light into the device structure with the help of microholes arranged in a lattice with a periodicity at the scale of wavelength. Vertically propagating light is coupled to the lateral modes in the material with periodic holes and absorbed efficiently despite a thin layer. More than 350% of EQE is enhanced by hole arrays compared to the case without holes up to 1700 nm wavelength. Such promising results enable Ge-on-Si photodiodes potentially cover both existing C band (1530 nm-1560 nm) and L band (1560 nm-1620 nm) and a new data transmission window (1620 nm-1700 nm), which can be a solution to capacity crunch of conventional standard single mode fiber (SSMF) cables. CMOS/BiCMOS compatible fabrication of photon-trapping Ge-on-Si photodiodes can lead to integrated transceiver circuits with electronics for cost-effective solutions in various near-infrared sensing applications such as metro and long haul dense wavelength division multiplexing (DWDM) systems, laser radar (LIDAR) systems, quantum communications and near-infrared imaging.

5:40pm **TF+EM+MI-WeA11 Correlating Composition and Structure with Optical Properties of Combinatorial Sputtered Thin Film Au_xAl_{1-x} Alloys***, **Robyn Collette**,* University of Tennessee Knoxville*; Y. Wu, J.P. Camden,* University of Notre Dame*; P.D. Rack,* University of Tennessee Knoxville

Surface plasmon resonances can be sustained by metallic nanostructures and have been explored for potential optoelectronic device applications. Superior plasmonic properties may be realized by alloying and consequently tuning the LSPR, however, there has been limited work done on alloys for use in plasmonic devices. The alloy behavior greatly depends on the ordering of the structure; thus, it is crucial to explore how the optical properties are related to the structure of the alloy.

In this work, the structure and optical properties of Au-Al thin film alloys were investigated as both individual metals have strong plasmon resonances. Initially, 350 nm thick Au_xAl_{1-x} ($0.15<x<0.72$) was co-sputtered on 100mm x 15mm silicon substrates. Subsequently samples of $0.9<x<1$ and $0<x<0.2$ were investigated. Energy dispersive spectroscopy (EDS) was used to measure the composition as a function of position on the substrate for the combinatorial samples. The crystal structure at various compositions were subsequently determined using grazing incidence x-ray diffraction (GIXRD) and the dielectric constants, ε_1 and ε_2, were determined via spectroscopic ellipsometry. The evolution of phases was studied by annealing various compositions under vacuum and the optical properties were correlated to observed phases on the equilibrium phase diagram. Lastly, we explore the plasmonic properties of lithographically patterned Au_xAl_{1-x} ($0 <x<0.2$). The optical transmission and reflection is measured and compared with electron energy loss spectroscopy results. The phase evolution is studied using a (scanning) transmission electron microscope with an *in situ* laser heating system and the low loss electron energy loss spectra are correlated to the structural changes. Interestingly, we found in the mixed phase region containing Al and $AuAl_2$ that as the concentration of $AuAl_2$ increased, an increase of ε_1 and a decrease of ε_2 around 1.5 eV.

6:00pm **TF+EM+MI-WeA12 The Multifunctional TiO2 Thin Films Sensor***, **Awais Ali**, M. Alam, S. Nasser, N. Akbar, A. Saeed, A.S. Bhatti,* COMSATS Institute of Information Technology, Islamabad Pakistan

In the present work, multifunctional/hybrid UV and IR sensing was performed by Nd doped TiO_2 thin films. Thin films were sputter deposited and concentrations of dopants was varied in targets. The results suggested that the incorporation of Nd produced compressional stresses in lattice, which resulted in textured growth and asymmetry of bonds as confirmed by XRD and Raman spectroscopy. The dopant driven non-stoichiometry and presence of O vacancies was evident from XPS measurements. The defects and dopant mediated luminescence was obtained in visible and IR regions, respectively. The sensing of UV light was attributed to the host (titania), whereas successful incorporation of dopant helped in sensing IR source.

2D Materials Focus Topic
Room 201B - Session 2D+EM+MI+MN+NS+SS-ThM
Novel 2D Materials

Moderator: Han Wang, University of Southern California

8:20am **2D+EM+MI+MN+NS+SS-ThM2 Controlled Growth of 2D Ni-Silicate and Silica Films on Ni$_x$Pd$_{1-x}$ (111) Substrates***, **Chao Zhou**, X. Liang, G.S. Hutchings, Z. Fishman, J.-H. Jhang, S. Hu, S. Ismail-Beigi, U.D. Schwarz, E.I. Altman,* Yale University

The discrete lattice constants and distinct chemical properties of different transition metal substrates hamper the systematic study of how the substrates can influence two-dimensional (2D) materials growth. The recent report of single-crystal epitaxial Ni-Pd alloy films with continuously tunable lattice constants open the possibilities to tackle this issue. Two-dimensional silica and transition-metal-doped silicate films prepared on metal substrates can be 2D analogues of porous bulk zeolites. In this research, 2D silica and Ni-silicate films were prepared on Ni$_x$Pd$_{1-x}$ (111) substrates under different growth conditions. After annealing in 2×10^{-6} Torr oxygen, Ni from the alloy substrates incorporates into the silica structure to form a crystalline 2D Ni-silicate structure, while an amorphous 2D silica bilayer can be observed after being annealed in 4×10^{-8} Torr oxygen. Density functional theory (DFT) was employed to model various silica and silicate phases on Ni$_x$Pd$_{1-x}$ (111) substrates. The results show that the 2D Ni-silicate films are thermodynamically stable on the substrates when the oxygen chemical potential is in the oxygen-rich range. In oxygen-deficient environments, 2D silica tends to form a stable Ni-free phase. With continuous control over the composition of NiPd alloy films, the surface strain applied on the Ni-silicate films through the lattice mismatch between the substrate and overlayer could also be continuously tuned. Only single-domain commensurate crystalline 2D Ni-silicate can be observed in zero or low-strain systems, while a second incommensurate crystalline domain which is rotated by 30° with respect to the commensurate domain can be observed when the lattice mismatch is over 1.85%.

8:40am **2D+EM+MI+MN+NS+SS-ThM3 Topological Materials***, **Hsin Lin**,* Institute of Physics, Academia Sinica **INVITED**

Topological materials host various novel quantum phases of electrons which are characterized by band topology and topologically protected surface/edge states. Despite recent progress, intense world-wide research activity in search of new classes of topological materials is continuing unabated. This interest is driven by the need for materials with greater structural flexibility and tunability to enable viable applications in spintronics and quantum computing. We have used first-principles band theory computations to successfully predict many new classes of topologically interesting materials, including Bi$_2$Se$_3$ series, the ternary half-Heusler compounds, TlBiSe$_2$ family, Li$_2$AgSb-class, and GeBi$_2$Te$_4$ family as well as topological crystalline insulator (TCI) SnTe family and Weyl semimetals TaAs, SrSi$_2$, (Mo,W)Te$_2$, Ta$_3$S$_2$, and LaAlGe family. I will also highlight our recent work on unconventional chiral fermions in RhSi and several material candidates for new TCI.

9:20am **2D+EM+MI+MN+NS+SS-ThM5 Few-Layer Rhenium Disulfide Synthesized Via Chemical Vapor Deposition***, **Michael Valentin**,* Army Research Laboratory*; A. Guan, A.E. Nguyen, I. Lu, C.S. Merida, M.J. Gomez,* University of California, Riverside*; R.A. Burke, M. Dubey,* Army Research Laboratory*; L. Bartels,* University of California, Riverside

Transition metal dichalcogenides (TMDs) are exciting new materials that have received much attention due to their semiconducting properties in the direct bandgap. Well-studied TMDs, such as molybdenum disulfide (MoS$_2$) and tungsten diselenide (WSe$_2$), exhibit a direct bandgap in the monolayer form, but an indirect bandgap in the bulk form. Rhenium disulfide (ReS$_2$), on the other hand, is a new TMD that is unique in its ability to retain a direct bandgap independent of thickness. By using chemical vapor deposition (CVD), few-layer ReS$_2$ is synthesized and characterized by optical methods such as Raman spectroscopy and photoluminescence. We also show characterization results for atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), transmission electron microscope (TEM), and electrical transport to determine thickness, crystallinity, homogeneity, and electrical characteristics for use in future flexible electronics.

9:40am **2D+EM+MI+MN+NS+SS-ThM6 Dipolar Disorder of a van-der-Waals Surface Revealed by Direct Atomic Imaging***, M.A. Susner,* Air Force Research Laboratory*; M.A. McGuire, **Petro Maksymovych**,* Oak Ridge National Laboratory

Recently, the family of transition metal thiophosphates –exhibiting ferroelecric, antiferromagnetic and correlated electron ground states – have gained attention as possible control dielectrics for the rapidly growing family of 2D and quasi-2D electronic materials [1]. Being van-der-Waals crystals, the surfaces of these materials can be created without dangling bonds, unlike those of complex oxides. Yet, because of robust insulating properties, the structure of their surfaces, the role of disorder, the structure of the topological defects in the order parameter and many other properties directly relevant to their prospective interfaces is almost entirely unknown.

Here we present the first atomically resolved imaging of CuScP$_2$S$_6$ s carried out using cryogenic non-contact atomic force microscopy. The surface exhibits good crystalline ordering at the atomic scale, revealing contrast on sub-unit cell level. The most remarkable property is long-range commensurate modulation of the surface morphology, with a topographic amplitude of only 2-3 pm. Combined with XRD analysis of the bulk and Monte-Carlo simulation of the Ising model on triangular lattice, we propose that the modulation arises from antiferroelectric polarization domains, albeit with frustrated long-range order. The key structural ingredient for this state is centrosymmetric position of Sc^{3+} within the layer, which forces the surrounding displacing Cu+1 ions to adopt a frustrated antiferroelectric state - in direct analogy frustrated magnetic systems. We will further discuss the peculiarities of nc-AFM imaging of this materials from the statistical analysis of the variation of images between scan, as well as the force-distance curve arrays. The possibility to directly visualize polar order opens broad opportunities to understand the atomistic aspect of ferroelectric, glassy and incommensurate phases in this material class, beginning with CuInP$_2$S$_6$ – which exhibits Curie temperature ~315K and giant negative electrostriction [2]. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. Microscopy experiments were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

[1] Susner Michael A., Chyasnavichyus Marius, McGuire Michael A., Ganesh Panchapakesan, and Maksymovych Petro, Advanced Materials **29**, 1602852 (2017).

[2] S. M. Neumayer, E. A. Eliseev, M. A. Susner, A. Tselev, B. J. Rodriguez, S. Jesse, S. V. Kalinin, M. A. McGuire, A. N. Morozovska, P. Maksymovych, and N. Balke, ArXiv:1803.08142 [Cond-Mat] (2018).

11:00am **2D+EM+MI+MN+NS+SS-ThM10 Advanced ARPES Analyzer and Momentum Microscope KREIOS 150 – Concepts and first results on layered materials and topological insulators***, **Paul Dietrich**, M. Wietstruk, T.U. Kampen, A. Thissen,* SPECS Surface Nano Analysis GmbH, Germany

Modern ARPES analyzers provide a high degree of parallelization in data acquisition, recording hundreds of energy and angle channels simultaneously. Additionally, integrated deflectors enable users to perform angle scanning perpendicular to the analyzer's entrance slit to record (k_x, k_y, E) data sets without sample rotation. However, the design of conventional analyzers implies a limited acceptance angle and corresponding accessible momentum space volume. Due to the trade-off between acceptance angle and angle resolution multiple changes in sample position and lens modes are necessary during a typical high resolution ARPES experiment. The new KREIOS 150 Energy Analyzer uses an extractor zoom lens design to overcome these limitations.

This new lens provides a full solid acceptance angle with highest angular resolution. In contrast to standard ARPES measurements with conventional hemispherical analyzers, electronic structure data from and beyond the 1st Brillouin zone is recorded without any sample movement. In addition the lens of such an instrument can work in a lateral imaging mode for microscopy as well. This enables navigation on the sample and reduces the size of the area under investigation in ARPES down to a few micrometers in diameter. This combination of large acceptance angle, high angular resolution and small acceptance area, makes this instrument the ideal tool for electronic structure studies on small samples or sample areas. The design is compact with a straight optical axis.

The capabilities of this instrument were tested at the UE 56/2 at the Bessy II synchrotron in Berlin. Specification tests show excellent angle and lateral resolution as well as small spot capability down to 2µm FOV. Subsequently real live samples like Graphene on Germanium were measured. Even on macroscopically rough surfaces like Graphene on $NbSe_2$ excellent ARPES and X-PEEM results could be obtained. By taking advantage of the small spot capability of the KREIOS 150 meaningful band structure data has been recorded on such patchy samples.

Acknowledgements: We thank Yu. Dedkov (University of Shanghai, China) and M. Fonin (University Konstanz) for providing beamtime and samples for the measurements with KREIOS 150 at BESSY II.

11:20am **2D+EM+MI+MN+NS+SS-ThM11 Carbon Nanomembranes with Sub-nanometer Channels: 2D Materials for Water Purification with High Selectivity and Highest Permeance***, Y. Yang, P. Dementyev, N. Biere, D. Emmrich, P. Stohmann, R. Korzetz, X.H. Zhang, A. Beyer, S. Koch, D. Anselmetti,* ***Armin Gölzhäuser,*** Bielefeld University, Germany

Clean water is a global challenge, and membrane filtration is a key technology to achieve it. Here, we report on carbon nanomembranes (CNMs) with sub-nanometer channels that prove to be excellent water filters, combining a high selectivity with an exceptionally high water permeance. The CNMs are fabricated via the cross-linking of terphenyl self-assembled monolayers [1], resulting in a ~1.2 nm thick membrane perforated by channels with diameters below ~0.7 nm and areal densities of $\sim10^{18}m^{-2}$. When tested as filter membranes, it was found that the CNMs efficiently block the passage of most gases and liquids [2]. However, water passes through, and it does this with a record-breaking permeance of $\sim1.1\times10^{-4}$ $mol\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-1}$. This suggests that water molecules translocate fast and cooperatively through the sub-nanometer channels.Assuming all channels in a TPT-CNMs are active in mass transport, we find a single-channel permeation of ~66 water molecules$\cdot s^{-1}\cdot Pa^{-1}$.We compare this with molecular transport through other carbon nanoconduits, such as carbon nanotubes or membrane proteins (aquaporins). As the fabrication of CNMs is scalable, their utilization opens a path towards the application of 2D-materials in energy-efficient water purification.

[1] A. Turchanin and A. Gölzhäuser: Carbon Nanomembranes, *Adv. Mater*. **2016,**28, 6075.

[2] Y. Yang, P. Dementyev, N. Biere, D. Emmrich, P. Stohmann, R. Korzetz, X. Zhang, A. Beyer, S. Koch, D. Anselmetti, A. Gölzhäuser, *ACS Nano*, in press.

11:40am **2D+EM+MI+MN+NS+SS-ThM12 Discovery of Dirac Monolayers and Elucidation of Functonalites by Advanced Soft X-ray Spectroscopy***,* ***Iwao Matsuda,*** University of Tokyo, Japan **INVITED**

Vapor deposition of three-dimensional (3-D) crystal on a substrate often results in formation of the novel 2-D materials with intriguing electronic states. The approach has been well-known in the field of "Surface Science", which has attracted our attentions over the past decades. Triggered by fabrication of the graphene layers, researches on such monatomic sheets have extended to various kinds such as silicene, germanene and so on. Soft X-ray spectroscopies, such as photoemission spectroscopy, have been used to directly probe electronic states of monatomic layers and also to examine carrier dynamics under the *operando* condition. We recently observed Dirac Fermions in a 2-D boron sheet, borophene, that forms spontaneously on the Ag(111) surface. Furthermore, we found pairing of the Dirac cones due to Moire-periodic perturbations of the overlayer-substrate interactions. In the Cu_2Si monolayer, we also discovered the 2-D Dirac nodal line fermions that are protected by the mirror reflection symmetry. In the presentation. I will describe details of our research on the novel 2-D Dirac materials and introduce the advanced soft X-ray techniques that reveal their functionalities for developing devices.

[1] B. Feng, IM *et al.*,Phys. Rev. Lett., **118**, 096401 (2017) .

[2] B. Feng, IM *et al.*,Adv. Mater. **30**, 1704025 (2018) .

[3] B. Feng, IM *et al.*,Nature Comm., **8**, 1007 (2017) .

Actinides and Rare Earths Focus Topic
Room 202C - Session AC+AS+SA-ThM

Nuclear Power, Forensics, and Other Applications

Moderator: Ladislav Havela, Charles University, Prague, Czech Republic

8:00am **AC+AS+SA-ThM1 Electron Microscopy in Nuclear Forensics***,* ***Edgar Buck****, D.R. Reilly, J.M. Schwantes, J.A. Soltis, T.Q. Meadows, D.A. Meier, J.F. Corbey,* Pacific Northwest National Laboratory **INVITED**

Recent advances in electron microscopy both in terms of spatial resolution, sensitivity, and the ability to perform in-situ chemistry experiments, present enormous opportunities to the nuclear forensic field. Extraction of specific particles of interest with dual-beam SEM-FIB instruments can be readily applied plutonium-contaminated materials. Furthermore, other developments in microscopy have enabled in-situ monitoring of interfacial processes and 3D tomographic views of specimens and phases. Several new advances in technology have enabled great advances and potential for nuclear science including nuclear forensics. These include dual-beam ion-electron systems for precise sample isolation and preparation, the electromagnetic lens aberration-corrector, high-count capacity x-ray detector systems, faster digital cameras, high performance electron backscattered diffraction systems in combination with 3D visualization tools, application of cryoTEM methods to material science, as well as micro-fabricated in-situ cells that enable direct observation of chemical and electrochemical processes in the EM. The application of these technologies to nuclear forensics will be discussed.

8:40am **AC+AS+SA-ThM3 New Frontiers with Fission Track Analysis and TOF-SIMS Techniques***,* ***Itzhak Halevy****,* Nrcn Israel*; R. Radus,* Ben Gurion University, Israel*; S. Maskova,* Charles University, Prague, Czech Republic*; A. Kogan, S. Samuha, D. Gridchin, E. Grinberg, E. Boblil, N. Haikin,* IAEC-NRCN, Israel*; I. Orion,* Ben-Gurion University -Negev, Israel*; A. Weiss,* Faculty of Engineering, Bar-Ilan University, Israel **INVITED**

Illicit trafficking of radioactive materials is known to exist from the early days of radioactive era. The nuclear forensics deals with recognizing the materials and processes of the radioactive industry. The properties of the materials can give a hint about the source of material and its original use.

The most common radioactive material involved in illicit trafficking is uranium. Uranium is a common natural element which can be found everywhere. The cosmogenic uranium is well known and defined. The natural enrichment of uranium is varying within a small range around 0.72 % and is indicative to its source. The enrichment of the anthropogenic uranium can vary much depending on the purpose and use of the material. Different enrichments are known for individual nuclear power plants, research reactors and military uses.

Measuring the uranium properties can indicate its enrichment, presence of other elements or impurities and can help in finding its attribution, namely its origin.

To learn more about the history of found material accurate isotopic measurements are needed.

The ratio between ^{230}Th and ^{234}U can give a good estimation of how much time passed from the last chemical cleaning of the material. This technique is called radio-chronometry or age dating.

We developed new Lexan detectors with much better signal to noise ratio to improve sensitivity and reduce the false alarm.

New Automated software can recognize the fission track (FT) automatically and give the parameters of the track, like: roundness, intensity, number of tracks and color histogram. In that program we can add ROI (region of interest) or to cancel a false positive FT identification.

Analytical equipment like TOF-SIMS (Time Of Flight - Secondary Ion Mass Spectrometry) and ICP-MS (Inductively Coupled Plasma - Mass Spectrometer located at the Geophysical survey Israel - GSI) together with new FTA software give new frontiers to the nuclear forensic research .

A microscope equipped with TOF-SIMS gives the ability to measure quantitatively, the ratio between the different isotopes and molecules. Using the scanning electron microscope, we are able to choose the desired particle which can be then analyzed using the TOF-SIMS. TOF-SIMS is a technique capable to distinguish not only between elements but also different isotopes. Knowing the ratio between the isotopes is very important as it can help us to classify the material looking for its possible origin. Morphology and depth profile than give other insight to the processes that the sample went through. Nano manipulators can extract the particle and transfer it to a different technique.

9:20am **AC+AS+SA-ThM5 Predictive Nuclear Forensics: Fundamental Frameworks to Fill Missing Pieces***,* ***Jenifer Shafer****, M. Koehl, A. Baldwin, D. Wu,* Colorado School of Mines*; R. Rundberg,* Los Alamos National Laboratory*; M. Servis,* Washington State University*; T. Kawano,* Los Alamos National Laboratory **INVITED**

Understanding the origin of nuclear forensic signatures provides the benefit of understanding how these signatures can be compromised and provides a framework to predict signatures that might arise under various conditions. The ability to predict signatures is particularly useful for the nuclear forensics community since only a limited number of samples exist. Frequently access to these samples can be further constrained due to classification boundaries. This talk provides two examples of how fundamental chemical and physical phenomena can be leveraged to understand signature origins, thus enabling a more robust nuclear forensics capability. The first study focuses on understanding how organic phase aggregation chemistry in the PUREX process can dictate trace metal, such as fission or corrosion product, partitioning patterns. By understanding how trace metals partition, information regarding the processing history, including the reprocessing site, could be ascertained. Trace metal partitioning patterns were studied by producing radiotracers in the USGS 1 MW TRIGA reactor. The influence of extractant aggregation on trace metal partitioning was then assessed using a combination of diffusion NMR spectroscopy and small angle neutron scattering. The second study focuses on understanding how cumulative fission product yields can describe the incident neutron energy. Fission yield curves of uranium-235 have a decrease in valley radionuclide production when the incident neutron energy is in the epithermal energy regime. This decrease in valley radionuclide production seems tied to the excitation of the uranium-236 to the 3- spin state. The octopule deformation of the 3- spin state enables more asymmetric fission than typically encountered with fast or thermal neutrons and thus suggests the structure of the excited uranium-236 compound nucleus could be, in part, responsible for cumulative fission product yields. These two studies highlight how fundmental science enables signature development.

11:00am **AC+AS+SA-ThM10 Soft X-ray Synchrotron Radiation Spectromicroscopy Studies of Radioactive Materials***, **David Shuh**,* Lawrence Berkeley National Laboratory*; A. Altman,* Lawrence Berkeley National Laboratory and UC Berkeley*; A.L.D. Kilcoyne, S.G. Minasian, J.I. Pacold, D.E. Smiles, T. Tyliszczak, D. Vine,* Lawrence Berkeley National Laboratory*; L. He, J. Harp, M. Meyer,* Idaho National Laboratory*; C. Degueldre,* University of Lancaster, Switzerland

Soft X-ray synchrotron radiation methodologies are being developed and employed at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory (LBNL) to elucidate the electronic structure of radioactive and actinide materials. Results from these investigations have begun to provide improved fundamental knowledge that can be used as a scientific basis for the enhanced design of actinide materials, complexes, ligands, and the overall understanding of actinide materials. The experimental developments at the ALS have centered on studies of radioactive materials with the soft X-ray scanning transmission X-ray microscope (STXM) at Beamline 11.0.2 for spatially-resolved near-edge X-ray absorption spectroscopy (XAS). The spectromicroscopy capabilities of the STXM provide the means to determine the speciation and composition in a range of actinide materials, particularly those of technological and environmental interest with spatial resolution that can reach to the true nanoscale. A particular emphasis has been on the use of light atom (B, C, N, O, F, Na, Mg, Al, Si) ligand K–edge XAS technique to determine the electronic structure characteristics in an array of unique and relevant materials. Furthermore, there are a host of additional electron energy level thresholds (such as the L–edges of the transition metals, the M–edges of the lanthanides, and others) that can be probed by near-edge XAS in the soft X-rays.

Recently, STXM spectromicroscopy studies have been extended to focused ion beam (FIB) prepared radioactive and irradiated material specimens in collaboration with Idaho National Laboratory. Future scientific developments and applications of soft X-ray spectromicroscopy investigations utilizing ptychography and in-operando methodologies will be discussed.

11:20am **AC+AS+SA-ThM11 Comparison of the Oxidation Rates for Alpha Versus Delta Plutonium by X-ray Photoelectron Spectroscopy***, **Art Nelson**, S.B. Donald, D.J. Roberts, W. McLean,* Lawrence Livermore National Laboratory

X-ray photoemission spectroscopy (XPS) was used to characterize differences in the oxidation rates for polycrystalline α-Pu versus δ-Pu related to variations in grain size and surface electronic structure. The evolution of the Pu 4f core-level chemical shift as a function of oxygen exposure at ambient temperature was quantified in oxidation profiles. In addition, the X-ray excited Pu NOO Auger line-shapes were combined with the chemical shift of the Pu $4f_{7/2}$ photoelectron line that defines the Auger parameter and results in a reliable method for determining oxidation states independent of binding energy calibration. The oxidation profiles reveal that α-Pu oxidizes faster than δ-Pu, both resulting in the $PuO_2/Pu_2O_3/Pu$ oxide structure. This data was used to a produce chemical state (Wagner) plot for select plutonium oxides.

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

11:40am **AC+AS+SA-ThM12 A Single-Stage AMS Detector for Secondary Ion Mass Spectrometry and its Applications to Nuclear Materials Analyses***, **David Willingham**, E.E. Groopman, K.S. Grabowski,* U.S. Naval Research Laboratory*; L. Sangely,* International Atomic Energy Agency*; A.P. Meshik, O.V. Pravdivtseva,* Washington University in St. Louis*; D.G. Weisz, K.B. Knight,* Lawrence Livermore National Laboratory

Secondary ion mass spectrometry (SIMS) has long been applied to the analysis of isotopic heterogeneities in nuclear materials. Few other methodologies can compete with the ability of SIMS to measure the isotopic composition of nuclear materials with high accuracy and precision with micrometer spatial resolution. Like many other mass spectrometry techniques, however, the presence of molecular isobaric interferences at any given mass-to-charge complicate interpretation of SIMS measurements. Uranium isotopes, for example, can be valuable and informative markers for the process of enriching uranium for nuclear fuel for the production of nuclear energy. In addition to the major uranium isotopes (^{238}U and ^{235}U), the minor isotope ^{236}U is of interest because it is an indication for the presence in the sample of uranium reprocessed from spent nuclear fuel. The resolving power needed to separate ^{236}U from the molecule $^{235}U^1H$, however, is greater than 38,000 - far beyond most the mass resolution of commercially available SIMS instruments. One solution to this problem is to use a Single-Stage Accelerator Mass Spectrometer (SSAMS) to accelerate secondary ions to a high enough energy (300keV) to enable molecular dissociation within a stripper gas while retaining good transmission, followed by SIMS-based detection. At the U.S. Naval Research Laboratory, we have developed the Naval Ultra-Trace Isotope Laboratory's Universal Spectrometer (NAUTILUS) to achieve this goal. Using the NAUTILUS, we accomplish molecule-free isotopic analysis of nuclear materials without sacrificing the benefits of SIMS. In this work, we demonstrate the broad applications of the NAUTILUS to areas of nuclear materials analyses including uranium bearing particle analysis for nuclear Safeguards, analysis of the Oklo natural nuclear reactor, and analysis of uranium doped silicate glasses as working reference analogs for nuclear fallout materials. The NAUTILUS represents a new era in SIMS analyses of complex materials with specific application to nuclear materials and general application to the SIMS community as a whole.

12:00pm **AC+AS+SA-ThM13 Physicochemical Properties of Ag in Annealed ZrN/SiC/Ag Heterostructures Used to Simulate TRISO Nuclear Fuels***, **Jeff Terry**, M. Warren, R. Seibert,* Illinois Institute of Technology

Silicon carbide (SiC) is used as a supportive and protective barrier in the cladding of tristructural-isotropic (TRISO) nuclear fuel particles. Previous studies both of surrogate surfaces and irradiated fuel have shown that the fission product silver (Ag) exhibits transport into and sometimes through the SiC barrier with temperatures above 500 °C. This silver release can cause safety concerns for maintenance workers due to plate-out on in-reactor components. Although an exact diffusion mechanism for Ag in SiC is unknown, a solution is needed to prevent this effect. The use of a ZrN protective coating may mitigate Ag transport and potential release. This study examines the transport of Ag in SiC through the use of surrogate multilayered thin-films. Thin films of subsequent layers of SiC, Ag, SiC, and ZrN deposited by pulsed-laser ablation deposition (PLD) under a range of annealing temperatures up to 1200 °C are studied. After heating, X-ray photoemission spectroscopy (XPS), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) was used to examine the surface of the ZrN. Initial results show that Ag does not readily diffuse through the ZrN layer like it does through SiC. The results and implications of this study will be discussed.

Applied Surface Science Division

Room 204 - Session AS+SE-ThM

Applied Surface Analysis of Novel, Complex or Challenging Materials

Moderators: Michael Brumbach, Sandia National Laboratories, Thomas Grehl, IONTOF GmbH, Germany

8:00am **AS+SE-ThM1 Understanding the Surface of Complex Oxides used in High Temperature Electrochemical Devices***, **John Kilner,*** Imperial College London, UK*; J.W. Druce,* International Institute for Carbon Neutral Energy Research (I2CNER), Japan*; H. Tellez, A. Staykov,* International Institute for Carbon Neutral Energy Research (I2CNER) **INVITED**

High temperature electrochemical devices, such as solid oxide fuel cells and electrolyzers, have been under development for application in clean energy systems for many years. Although acceptable performance can be achieved, the requirements of low cost and high durability have been a major hurdle to commercialization. This has necessitated a lowering of the operating temperature from circa 800-900ºC, to temperatures in the region of 500-600ºC, with a consequent loss of electrochemical activity of the electrodes, particularly the air electrode. Key to optimizing performance is gaining an understanding of the gas/solid interface between the Mixed Ionic Electronic Conducting (MIEC) electrodes and the oxygen-rich ambient, and how the structure, composition and activity evolves with time. We have used a multifaceted approach to probe the surfaces of ceramic mixed conductors, after treatment in typical SOFC cathode operating conditions. This has involved ion beam based techniques such as Low Energy Ion Scattering (LEIS) to sample the composition of the outermost atomic layers of ceramic materials, Secondary Ion Mass Spectrometry (SIMS) to measure oxygen exchange activity, complemented by Density Functional Theory (DFT) to clarify possible mechanisms.

The surface termination of substituted (AA')(BB')O_3perovskite-based MIEC materials, such as $La_{1-x}Sr_xCo_{1-y}Fe_yO3\text{-}\delta$ (LSCF), has been studied using LEIS [1] and shown to be dominated by A cations and oxygen, and in particular by segregation of the Sr substituent. For selected (AA')(BB')O_3 compositions, we have investigated the rate of oxygen exchange and shown changes in surface activity that are related to changes in surface chemistry. We have used the knowledge gained from experiment to guide theoretical investigations, to aid in the optimization of candidate air electrode materials. This theoretical study was performed using DFT to simulate the interaction of an oxygen molecule with representative AO and A'O segregated surfaces [2,3].

This combination of theoretical studies guided by advanced surface analysis techniques (i.e. LEIS and SIMS) is enhancing our understanding of processes which determine the performance of these important clean energy devices.

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8:40am **AS+SE-ThM3 Vectorial Method used to Monitor a XPS Evolving System: Titanium Oxide Thin Films under UV Illumination***, S. Bechu,* Institut Photovoltaïque d'Ile-de-France*; N. Fairley,* Casa Software Ltd, UK*; L. Brohan,* Institut des materiaux Jean Rouxel, France*; **Vincent Fernandez,*** Université de Nantes, Institut des matériaux Jean Rouxel, France*; M. Richard-Plouet,* Institut des matériaux Jean Rouxel, France

1. Introduction

Third generation solar cells aims at increasing efficiency to overtake the 31% theoretical efficiency of simple junction photovoltaic cells established by Shockley and Queisser . According to Marti and Luque [1] , intermediate band cell concept could increase the photocurrent via the absorption of sub-bandgap photons without degrading the voltage. In this perspective, we developed hybrid photosensitive sols-gels based on titanium complexes with specific optical and electronic properties [2] . Once illuminated under UV light, an intermediate band (IB) appears in the band structure so the absorption spreads over visible to near infrared due to reduction of Ti(IV) in Ti(III) [3] and leads to several important changes in the titanium oxide based nanomaterial chemistry. Thanks to this absorption range increase, these gels could be used as active layers in solar cells.

2. Analysis applied to characterize chemical modifications

In order to get insight in the chemical modifications induced by the creation of the IB, XPS experiments were conducted on thin films while UV illumination was performed *in situ*. We present here a new mathematical method which can be applied to XPS measurements when an evolving set of data is recorded: the vectorial method [4,5]. In this case this method is applied simultaneously to Ti 2p and O 1s XPS peaks [6]. From the data set analysis, we established that each of the two Ti(IV) and Ti(III) signals can be split into two components: one Ti(IV) at 458.4 eV is associated to one Ti(III) at 457.1 eV whereas, under UV illumination, a second Ti(IV) peak appears and evolves similarly than a second Ti(III) peak, at 458.1 and 456.7 eV respectively. Those features were obtained from the vectorial method. It was successfully applied to *in situ* UV illumination allowing to get the percentage of thin films photoreduction, the chemical state appearing upon illumination and evolution.

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9:00am **AS+SE-ThM4 XPS Characterization of Copper and Silver Nanostructures***, **Tatyana Bendikov,** M.D. Susman, F. Muench, A. Vaskevich, I. Rubinstein,* Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS) is uniquely suited for the direct characterization of nanomaterials in terms of elemental composition, chemical and electronic states of the elements and thin layer thicknesses. Here we present examples where XPS analysis provides critical information for understanding the growth and oxidation mechanisms of metal nanostructures.

Studies of solid-state oxidation of copper nanoparticles (NP) by in-situ plasmon spectroscopy complemented by electron microscopies showed formation of oxide/(metal+void) core-shell structure.[1] XPS analysis allows us to unambiguously identify the presence of both CuO and Cu_2O phases in the oxide shell, and to calculate the relative thicknesses of each layer. These data, in combination with electrochemistry, provide proof for a quantitative model of Cu NPs oxidation.

In a recent study, we investigated the mechanism of the electroless formation of nanostructured silver nanoplatelet (NPL) films in the presence of a Fe(III)-tartrate complex.[2] Electron microscopy and XRD showed that NPLs are formed by secondary nucleation on the edges, while nucleation on the flat (111)-oriented faces is suppressed. XPS analysis of NPLs confirmed strong Fe(III)-tartrate adsorption to the Ag NPS surface. XPS studies of the Fe chemical environment reveal the possible formation of polymeric complexes in the adsorbed layer, which may explain the almost complete inhibition of secondary nucleation on the flat (111) surfaces of Ag NPLs.

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*Prof. Israel Rubinstein deceased on October 21, 2017.

9:20am **AS+SE-ThM5 Quantification of Hydroxyl, Major Element and Trace Element Concentrations in Oxide Glasses by Quadrupole SIMS.***, **Albert Fahey,** A.R. Sarafian, T. Dimond,* Corning Inc.

Major and trace element calibrations have been established for positive and negative secondary ions measured by Quadrupole SIMS. A Cs+ primary ion beam is used exclusively and element secondary ions are measured directly, not by the MCs+ method. This affords greater sensitivity and is better matched to the operating characteristics of a quadrupole mass spectrometer than by using MCs+ for positive ion species only. Both natural well-studied geologic glasses and Corning research glasses that have been thoroughly characterized have been used to establish the calibrations.

The CAMECA 4550 Quadrupole SIMS is well-suited to measurement of oxide glasses. Charge-compensation is easily achieved for a Cs+ primary beam on uncoated samples of almost any size. This allows the measurement of concentration of species in the surface of glass (from a few nanometers to several micrometers) that can have a significant impact on the physical and chemical durability of the glass. Because oxide glasses contain oxygen as their major element both positive and negative ions can be generated by sputtering with Cs. Although the use of a Cs primary ion beam is generally associated with measurement of negative secondary ions or the use of MCs+ secondary ions, the presence of oxygen in the glass allows production of a significant quantity of positive ions yielding linear calibrations for species that typically would produce positive secondary ions with an oxygen primary beam. Of course, secondary negative ions are produced as well and for the appropriate elements and small molecular ions yield linear calibrations as well.

Detection limits and details of the calibrations will be shown and discussed and examples-measurements of near surface composition changes in various oxide glasses will be shown. Connections of surface chemistry to other glass-properties will be made and explained.

9:40am **AS+SE-ThM6 Modification of Sputtered Carbon Surfaces in Biosensor Arrays*, Varun Jain,* *M.R. Linford,*** Brigham Young University

We describe the chemical modification of carbon surfaces with an eye towards employing them in biosensor (DNA) arrays. Carbon was deposited in thin film form by DC and HIPIMS magnetron sputtering. These depositions were confirmed by atomic force microscopy step height measurements. As indicated by X-ray photoelectron spectroscopy (XPS), the resulting material contained some oxidized carbon at its surface, including –COOH type moieties. These groups could be directly activated for amine attachment using a combination of a carbodiimide (EDC) and sulfo -N-hydroxysuccinimide. Direct attachment of a variety of amines was then possible on this surface, where this process could be followed through the N 1s XPS signal. The surfaces were also activated by direct chlorination using PCl_5, where this process could again be followed by XPS – XPS revealed the introduction and disappearance of chlorine. That is, the chlorine on the resulting carbon surfaces could be nucleophilically replaced with a variety of amines. The DC and HIPIMS sputtered carbon films showed different numbers of reactive functional groups, and the HIPIMS carbon shows unusually smoothness and density by scanning electron microscopy.

11:00am **AS+SE-ThM10 The Role of Surface Analysis in Characterization of Synthetic Opioids: TOF-SIMS imaging of Fentanyl and Fentanyl Analogs for Forensics and First Responder Safety*, Greg Gillen,*** *S. Muramoto, J. Verkouteren, E. Sisco,* National Institute of Standards and Technology (NIST)

The misuse and addiction to opioids including heroin and synthetic opioids such as fentanyl and its various analogs has become a national crisis. Drug overdoses have become the leading cause of death for Americans under the age of 50 with 64,000 overdose related deaths in 2016. The extreme potency of fentanyl and its analogs (100-10,000 times more potent than morphine) may result in even very small doses causing life threatening overdoses. The potency is also a safety concern due to the potential for accidental exposure of law enforcement, first responders, forensic lab personnel and health care providers. To address this concern, several trace chemical analysis techniques are being evaluated as presumptive methods for identification of a suspected opioid while minimizing exposure to end users (1). In addition, since the bulk of illicitly manufactured fentanyl enters the US via overseas mail, there is interest in application of the same chemical screening techniques for detection of fentanyl residues on packages to support interdiction. To facilitate the continued development, evaluation and optimization of the aforementioned screening tools, TOF-SIMS imaging and mass spectral analysis is being used to characterize the particle size and chemical composition of fentanyl and related compounds produced by solution casting of pure materials onto metal substrates or as particles collected on conductive adhesive tapes after sampling the outsides of packages containing suspected opioids. TOF-SIMS was able to image and provide unique mass spectral signatures from individual particles of heroin, fentanyl and several analogs. In order to increase the sensitivity of TOF-SIMS for particle identification, we have evaluated the use of acidic polymer substrates (Nafion) as proton donating particle collection substrates. Preliminary results suggest orders of magnitude improvements in protonated secondary ion signals for fentanyl. Finally, the screening technologies being developed were not designed with consideration of the significant toxicity of fentanyl and fentanyl analogs in the form of respirable aerosols. In a typical screening analysis, thermal desorption from a collection swipe can lead to the formation of aerosols in micrometer size range posing a possible risk of toxic exposure to the analyst. TOF-SIMS was also used to characterize the size distribution of thermally desorbed aerosols emitted by these techniques.

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11:20am **AS+SE-ThM11 3D TOF SIMS, Parallel Imaging MS/MS, and XPS Analysis of Glitterwing (*Chalcopteryx rutilans*) Damselfly Wings*, Ashley Ellsworth,*** *D.M. Carr, G.L. Fisher, B.W. Schmidt,* Physical Electronics*; W.W. Valeriano, W.N. Rodrigues,* UFMG, Brazil

The male Amazonian glitterwing (*Chalcopteryx rutilans*) damselfly has transparent anterior wings and brightly colored iridescent posterior wings. The colors are important for damselflies with regard to sexual recognition, mating, and territorial behavior. The source of the varying colors was determined by Valeriano [1] using electron microscopy and optical reflectance to analyze the internal microstructures. SEM and TEM images revealed that the iridescent wings have multiple alternating layers with different electronic densities. The colors span the visible spectrum with red, blue, and yellow/green regions on the wings. Measurement of the thickness and number of layers is readily achievable by electron microscopy, however it is unable to characterize the chemistry of the different layers giving rise to these natural photonic crystals.

TOF-SIMS is a well-established technique for analyzing the elemental and molecular chemistry of surfaces. TOF-SIMS can be used to probe the 3D structure and chemistry of a wide variety of organic and inorganic materials, both synthetic and naturally occurring, due to the advent of cluster ion beams such as C_{60}^+ and large cluster Ar_n^+. With the recent addition of MS/MS capabilities, a conventional TOF-SIMS (MS1) precursor ion analysis and tandem MS (MS2) product ion analysis of targeted precursor ions may be acquired simultaneously and in parallel. The parallel imaging MS/MS is a powerful tool allowing for unambiguous peak identification and provides the maximum information from a given analytical volume.

Here, we explore the use of MS/MS to characterize the chemical composition of the waxy cuticle present on the outer surface of the damselfly wing. We will present results of 3D TOF-SIMS analyses for both transparent and colored wings to correlate with the electron microscopy and optical results to further the understanding of these natural photonic crystals. [2] Further, we will compare and contrast XPS large cluster Ar_n^+ depth profiling results to reveal the complementary nature of the two techniques.

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11:40am **AS+SE-ThM12 Characterization of Aniline Dyes in the Modern Colored Papers and the Prints of José Posada***, J.K. Hedlund, L.D. Gelb,* ***Amy Walker,*** University of Texas at Dallas

José Posada was a Mexican artist active during the turn of the 20th century, and is often called the father of modern Mexican printmaking. Many of his prints ("broadsides") have vivid colors but are in urgent need of repair. The dyes that give these broadsides their colors are aniline dyes which are soluble in many solvents. Solvents are often used in paper conservation for the removal of pressure-sensitive tapes, and so treatment protocols that preserve these colors are needed. To develop these methods the aniline dyes need to be identified and characterized.

Dye identification requires either non-destructive *in situ* techniques, such as Raman spectroscopy, or *ex situ* techniques with very high sensitivity; only extremely small samples can be taken in order to preserve the integrity and appearance of the broadsides. Although Raman spectroscopy has been employed to analyze Posada prints it has only limited success especially in the analysis of blue and yellow dyestuffs.

We present a new strategy for analyzing dyed paper samples using secondary ion mass spectrometry (SIMS) and analysis of the resulting data using maximum *a posteriori* (MAP) reconstruction. To test our protocol, we first characterized modern cotton paper colored with a range of aniline dyes. Subsequently we analyzed fiber samples taken from Posada prints. Using SIMS, we are able to identify the dyes used in Posada prints, including hitherto unidentified blue and yellow dyes. Furthermore, MAP analysis provides not only unambiguous identification of the dye adsorbed in the paper by comparison with pure-dye reference samples, but also the characteristic mass spectrum of the paper itself.

12:00pm **AS+SE-ThM13 GaAs and Si Surface Energies derived from Three Liquid Contact Angle Analysis (3LCAA), as a Function of Oxygen Coverage for Heterogeneous Nano-Bonding^{TM}**, ***Sukesh Ram,*** Arizona State University; *K.L. Kavanagh,* Simon Fraser University, Canada; *F.J. Ark, C.E. Cornejo, T.C. Diaz, M.E. Bertram, S.R. Narayan, J.M. Day, M. Mangus, R.J. Culbertson, N. Herbots,* Arizona State University; *R. Islam,* Cactus Materials, Inc.

Native oxides used as surface passivation during semiconductor processing hinder the formation of high quality epitaxial layers. In this research, the surface energies and oxygen content of native oxides of Si(100) and GaAs(100) are measured before and after surface processing prior to a wafer bonding process at T<220°C, “NanoBonding™” [1,2]. Based on Van Oss’s theory, Three Liquid Contact Angle Analysis (3LCAA) yields the total surface energy, γ^T, of semiconductors and insulators. Van Oss models γ^T as combining of molecular interactions or “Lifshitz-Van der Waals” energy γ^{LW} with the energy of interaction with electron donors, γ^+,and acceptors, γ^-. A new automated image analysis algorithm, “Drop and Reflection Operative Program”(DROP), enables fast, accurate and reproducible extraction of contact angles without subjectivity, reducing to <1° the typical ~5° error between contact angles measurements due to manual extraction. Using for each wafer, a minimum of 12 to 30 drops yields 48 to 120 contact angles, yielding γ^T , γ^{LW}, γ^+ and γ^- with accuracies better than 3%. By using Ion Beam Analysis (IBA) combining <111> channeling in (100) crystals with the 3.039 ± 0.01 MeV (^{16}O, ^{16}O) nuclear resonance, oxygen coverage can be measured with ML accuracy before and after processin, via SIMNRA simulations, correlating oxygen coverage to data within 1%.

Boron-doped p^-Si(100) is found to be always hydrophilic pre-etch, with a γ^T of 53 ± 1.4 mJ/m^2. After an aqueous HF (1:20) etch, γ^T decreases 10% to 48 ± 2.6 mJ/m^2, and Si is hydrophobic. GaAs(100) is initially always very hydrophobic with a γ^T of 37 ± 2.0 mJ/m^2. After etching, Te-doped n+GaAs always becomes hydrophilic with a γ^T increase of 50% to 66 mJ/m^2 ± 1.4 mJ/m^2. Native oxides on B-doped p^-Si(100) wafers are found by IBA to contain 13.3 x 10^{15} at/cm^2 or 13.3 ± 0.3 oxygen monolayers (ML). After an aqueous HF (1:20) etch, Si(100) exhibits only a 11.6 ± 3% reduction in oxygen to 11.8 ± 0.4 ML . GaAs native oxides contain 7.2 ± 1.4 oxygen ML. After a proprietary passivation-based etch, GaAs native oxides are reduced 49.1 ± 4% to 3.6 ± 0.2 oxygen ML without change in GaAs surface stoichiometry.

3LCAA can quantify accurately the reactivity of a surface before Nano-Bonding^{TM}, which can be correlated to oxygen coverage and structure. High-resolution IBA and 3LCAA allows for a quantitative analysis of Si and GaAs surfaces energies as function of surface processing, enabling for the engineer interactions between surfaces for NanoBonding.

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Biomaterial Interfaces Division
Room 101B - Session BI-ThM

Biomolecules and Biophysics at Interfaces

Moderator: Joe Baio, Oregon State University

8:00am **BI-ThM1 Bioinspired Adaptive Reconfigurable Material Systems based on Smart Hydrogels**, ***Ximin He,*** University of California, Los Angeles **INVITED**

From the cellular level up to the body system level, living organisms cooperatively sense to adapt to or self-regulate the local environment, and can also harvest energy from the environment to keep alive and perform various functionalities. These graceful capabilities arise from the chemo-mechanical actions that transform the molecular configuration changes to micro/macroscopic mechanical motions, in response to environmental cues. Inspired by these unique adaptive abilities, we have developed a series of adaptive material systems, which are based on stimuli-responsive hydrogels capable of adaptively reconfiguration. This presentation will introduce three novel functionalities that this broad-based platform has demonstrated, including ultrafast optical sensing of chemical and biological species and autonomous regulating of local conditions. Living organisms ubiquitously display colors that adapt to environmental changes, relying on the soft layer of cells or proteins. Inspired by this strategy, we created a simple and universal adaptive color platform based on a hydrogel interferometer (*Adv. Mater.* 2018). Such interference colors provide a visual and quantifiable means of revealing rich environmental metrics. The single material-based platform has advantages of remarkable color uniformity, fast response, high robustness, and facile fabrication. Its versatility has been demonstrated by diverse applications: a volatile-vapor sensor with highly accurate quantitative detection, a colorimetric sensor array for multi-analyte recognition, breath-controlled information encryption, and a colorimetric humidity indicator. Portable and easy-to-use sensing systems are demonstrated with smartphone-based colorimetric analysis. Second, based on this platform, we further realized a novel function - fully autonomous separation of target molecules from a mixture fluid such as wastewater or biofluid.

8:40am **BI-ThM3 Importance of a In Depth Characterisation for the Design of Functional Gold Nanoparticles for Bioapplications**, *R. Capomaccio, I. Ojea-Jimenez, D. Mehn, P. Colpo, D. Gilliland,* European Commission - Joint Research Centre, Italy; *R. Hussain, G. Siligardi,* Diamond Light Source Diamond House, Harwell Science and Innovation Campus, UK; *L. Calzolai,* ***Giacomo Ceccone,*** European Commission - Joint Research Centre, Italy

The design and fabrication of functionalized nanoparticles (NPs) are of great interest in biotechnology and biomedicine, especially for diagnostic and therapeutic applications.[1] However, at the moment the challenges related to the characterization of complex, multi-functional nanoparticles are still hampering the development of advanced bio-nano-materials.[2,3] In particular the interaction of NPs with protein has been the subject of many investigations in the last years and although important advances were made, several important issues (e.g. thermodynamic constants, protein structure changes) are still not completely understood.[4-6]

In this work, the interaction of gold nanoparticles (AuNPs) with human serum albumin (HSA) has been investigated as model system. First a simple method to determine the structure and morphology of the AuNPs-HSA complexes will be described.[7] Then the interaction of HSA with a model system consisting of AuNPs functionalized with two differentially-terminated poly(ethylene oxide) ligands, providing both “stealth” properties and protein-binding capabilities to the nanoparticles have been investigated. In particular, the purpose of this study was to: i) monitor and quantify the ratios of ligand molecules per nanoparticle; ii) determine the effect of coating density on non-specific protein adsorption; iii) to assess the number and structure of the covalently-bound proteins. For this a combination of techniques, including Centrifugal Liquid Sedimentation, Dynamic Light Scattering, Flow Field Flow Fractionation, Transmission Electron Microscopy, Circular Dichroism, XPS and ToF-SIMS have been employed to compare complementary outcomes from typical and orthogonal techniques used on nanoparticle characterisation.[8]

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9:00am **BI-ThM4 A Model Membrane Microsystem for Measurement of the Kinetics of Transmembrane Proton Transport***, J.P. Madsen, A. Johnson, M.L. Cartron, N.C. Hunter, S.P. Armes,* ***Graham Leggett,*** University of Sheffield, UK

Binary brush structures consisting of poly(cysteine methacrylate) (PCysMA) "corrals" enclosed within poly(oligoethylene glycol methyl ether methacrylate) (POEGMA) "walls" are fabricated simply and efficiently using a two-step photochemical process. First, the C-Cl bonds of 4-(chloromethyl)phenylsilane monolayers are selectively converted into carboxylic acid groups by patterned exposure to UV light through a mask and POEGMA is grown from unmodified chlorinated regions by surface-initiated atom-transfer radical polymerization (ATRP). Incorporation of a ratiometric fluorescent pH indicator, Nile Blue 2-(methacryloyloxy)ethyl carbamate (NBC), into the polymer brushes facilitates assessment of local changes in pH using a confocal laser scanning microscope with spectral resolution capability. Moreover, the dye label acts as a radical spin trap, enabling removal of halogen end-groups from the brushes via *in situ* dye addition during the polymerisation process. Second, an initiator is attached to the carboxylic acid-functionalised regions formed by UV photolysis in the patterning step, enabling growth of PCysMA brushes by ATRP. Transfer of the system to THF, a poor solvent for PCysMA, causes collapse of the PCysMA brushes. At the interface between the collapsed brush and solvent, selective derivatisation of amine groups is achieved by reaction with excess glutaraldehyde, facilitating attachment of aminobutyl(nitrile triacetic acid) (NTA). The PCysMA brush collapse is reversed on transfer to water, leaving it fully expanded but only functionalized at the brush-water interface. Following complexation of NTA with Ni^{2+}, attachment of histidine-tagged proteorhodopsin and lipid deposition, light-activated transport of protons into the brush structure is demonstrated by measuring the ratiometric response of NBC in the POEGMA walls.

9:20am **BI-ThM5 Theranostics Gold Nanoparticles for Brain Cancer Applications***, I. Naletova, L.M. Cucci, F. D'Angeli, C.D. Anfuso, G. Lupo,* University of Catania, Italy*; A. Magrì,* National Council of Research (CNR), Italy*; C. Satriano,* University of Catania, Italy*;* ***Diego La Mendola,*** University of Pisa, Italy

In this work, hybrid assemblies of plasmonic gold nanoparticles (AuNPs) and peptides mimicking the putative cell binding domain of angiogenin protein (60-68 sequence)[1] were investigated in their interaction with artificial membranes of supported lipid bilayers (SLBs) and cellular membranes of cancer cell lines. In particular, the response of glioblastoma cell line (A172), as model of the most aggressive cancer that begins within the brain[2], and neurons obtained by differentiated neuroblastoma cell line (SHSY5Y), as 'normal cells', was scrutinized. The influence of copper, which is a pivotal co-player of cellular homeostasis in both physiological and pathological angiogenesis, was investigated in parallel with the gold nanoparticles functionalized with a fluorescent derivative of Ang(60-68) peptide. Control experiments using the non-fluorescent peptide analogous immobilized onto the AuNPs either by physisorption (Ang(60-68)) or chemisorption (Ang(60-68)Cys) were also included. The hybrid peptide/AuNP/copper systems were characterized by means of UV-visible, AFM and CD, to address the plasmonic changes, the nanoparticle coverage and conformational features at the hybrid biointerface. Lateral diffusion measurements on SLBs after their interaction with the peptide-functionalised AuNPs pointed to a stronger membrane interaction in comparison with the uncoated nanoparticles. Cell viability and proliferation assays indicated significant differences, in the presence or absence of copper, for the two cell lines. Cell imaging by confocal microscopy evidenced dynamic processes modulated in a synergic way by the different components (peptide, gold nanoparticle, copper) of the hybrid nanoplatforms at the level of the cell membrane (cytoskeleton features observed by actin staining) as well as at the sub-cellular compartments (copper-binding proteins).

[1] Cucci LM, Munzone A, Naletova I, Magrì A, La Mendola D, Satriano C. *Biointerphases*. 2018;13(3):03C401.

[2] Bleeker FE, Molenaar RJ, Leenstra S. Recent advances in the molecular understanding of glioblastoma.*J Neurooncol.* 2012;108(1):11-27.

11:00am **BI-ThM10 Non-equilibrium Thermodynamic Model for DNA at Nanochannel Junctions***,* ***Saroj Dangi,*** North Carolina State University

DNA, often studied as a polymer molecule, extends along the axis of confining channel if the size of channel is less than the radius of gyration of the molecule. Extended molecule can be manipulated for wide range of applications such as DNA sorting, gene mapping, single molecule experiment, and fundamental polymer physics experiment. The optimization and advancement of these nanofluidic applications necessitates the understanding of physics behind the confinement of DNA in nanochannel. So far, most of the studies have considered linear and uniform channels. However, many nanofluidic applications such as sorting, single molecule experiment require complex manipulation of DNA in branched channels with junctions. Dynamics response of DNA in such nanofluidic networks with junctions and asymmetric channels is relatively unknown. We studied the transport of DNA in a nanofluidic device made up of series of nanochannel junctions with asymmetric channel size. Here we present a non-equilibrium thermodynamic model for a nanochannel junction with asymmetry in channel size. We show that the transport direction of DNA in the device can be tuned locally by altering the confinement free energy of DNA or the flow potential in nanochannels. Using our model, we show that the motion of DNA in branched nanofluidic networks can be predicted stochastically.

11:20am **BI-ThM11 Dipeptide Nanocontainers Immobilised on Graphene Nanoplatforms for Drug-delivery Applications***, V.C.L. Caruso,* University of Catania, Italy*; G. Trapani,* University of Catania and Scuola Superiore di Catania, Italy*; L.M. Cucci, I. Naletova,* University of Catania, Italy*; D. La Mendola,* University of Pisa, Italy*;* ***Cristina Satriano,*** University of Catania, Italy

Graphene oxide (GO) nanosheets, owing to their high surface-to-volume ratio and the richness of oxygen-containing moieties (including carboxyl, hydroxyls and epoxide groups) represent ideal 2D nanoplatforms for drug delivery applications [1]. The integration of GO with homo-aromatic dipeptides, which are able to self-assemble into ordered structures such as nanotubes and nanowires [2], may offer unique potentialities at the biointerface because of the increased biocompatibility of the hybrid system and, remarkably, for the capability to load/protect a cargo into the peptide nanocontainers. Moreover, metal ions can influence/drive the peptide self-assembling process as well as to induce additional properties of the hybrid system (e.g., antibacterial and angiogenic properties in the case of Cu^{2+}ions [3]).

In this work, the hydrophobic dipeptides Phe-Phe (FF) and Tyr-Tyr (YY) were grown in the presence of graphene oxide (GO) and copper ions, to fabricate hybrid peptide-GO-metal nanoassemblies with multifaceted features.

The nanoassemblies were scrutinised spectroscopically (UV-visible, fluorescence and circular dichroism) and microscopically (atomic force microscopy and confocal microscopy). Quartz crystal microbalance with dissipation monitoring (QCM-D) was used for real-time acoustic sensing of the interaction of the hybrid nanoplatforms with supported lipid bilayers, used as model cell membranes. Promising results of cellular uptake in neuroblastoma cells were measured by confocal microscopy for the assemblies loaded with the anticancer drug doxorubicine.

[1] Consiglio, G., Di Pietro, P., D'Urso, L., Forte, G., Grasso, G., Sgarlata, C., ... & Satriano, C. (2017). Surface tailoring of polyacrylate-grafted graphene oxide for controlled interactions at the biointerface. *Journal of colloid and interface science*, *506*, 532-542.

[2] Reches, M., & Gazit, E. (2003). Casting metal nanowires within discrete self-assembled peptide nanotubes. *Science*, *300*(5619), 625-627.

[3] Yu, L., Jin, G., Ouyang, L., Wang, D., Qiao, Y., & Liu, X. (2016). Antibacterial activity, osteogenic and angiogenic behaviors of copper-bearing titanium synthesized by PIII&D. *Journal of Materials Chemistry B*, *4*(7), 1296-1309.

11:40am **BI-ThM12 Seriatim Operando STM and FTIR Study of Phospholipid Membrane Phase Transition Driven by Electrochemical Potential Control***,* ***Taro Yamada,*** RIKEN, Japan*; S. Matsunaga, H. Shimizu,* The University of Tokyo*; T. Kobayashi,* RIKEN, Japan*; M. Kawai,* The University of Tokyo

Phospholipid (1,2-dialkanoyl-sn-glycero-3-phosphocholine, DHPC for alkyl=C_6H_{13}, DDPC for $C_{10}H_{21}$) monolayers were prepared on 1-octanethiol-terminated gold surface, as a model of biological cell membrane, and nanoscopically observed by electrochemical scanning tunneling microscopy (EC-STM) and internal multiple reflection Fourier-transformed infrared absorption spectroscopy (FTIR) within aqueous electrolytic solutions. This dual-technique in situ operando observation revealed structural changeover of the phospholipid membrane according to the applied electrode potential. In 0.05 M NH_4ClO_4 solution (pH 7.0) at 0 V vs RHE, DHPC monolayer was a fluidic monolayer along the underlying thiol monolayer, with mobile chasms through which underlying vacancy islands of the substrate were frequently seen.by application of -0.2 V, the monolayer was slowly converted into solid striped structure. This is designated as “hemimicellar aggregation” [1] with a periodicity of 4.3 nm, and observed also for DDPC. By returning the substrate potential, the lipid monolayers restored fluidic phase. This transition was reversible and repeatable. By application of +0.2 V the fluidic feature was maintained despite a slight increase of monolayer height. When the potential was swept from +0.2 V to -0.2 V, elliptic agglomerates with an average diameter of 13 nm was observed. After this, the hemimicellar aggregation was never observed by any kind of potential cycling. This irreversible change of phase coincided with the seriatim FTIR observation, using deuterium-labelled DHPC molecules. The initial change of fluidic to hemimicellar did not exhibit drastic change in IR spectra, except a reversible splitting of the P-O stretching in the region of 1200-1300 cm-1. After application of +0.2V DHPC with the head-group choline part $(-C_2D_4N^+(CD_3)_3)$ was lost as a surface IR signal. This is an evidence for irreversible dissociation of DHPC into choline and phosphatidyl acid. The elliptic grains correspond to the phosphaticyl acid, differently agglomerated from that of intact DHPC hemimicelles. The potential shift of this amplitude is similar to the membrane potential of real cells. It is seen that phospholipid molecules, the robust solid component of cell membrane, can be easily involved chemical reactions under such membrane potential by the aid of membrane proteins for example. This series of experiment also demonstrates the applicability of seriatim surface observation techniques such as IR spectroscopy in addition to STM, which does not always distinguish the molecular species and detect chemical reactions.

[1] J. Am. Chem. Soc. 126 (2004) 12276.

12:00pm **BI-ThM13 Mitochondria Localized Polymerization for New Cancer Therapy**, ***Ja-Hyoung Ryu**,* Ulsan Natioanl Institute of Science and Technology, Republic of Korea

Recently, targeting mitochondria, the vital organelle for cell survival, as it plays a central role in energy production and apoptotic pathways, has been recognized as an efficient strategy in different therapeutic techniques by disturbing the normal function. Specifically, the conjugation of drug to triphenylphosphonium (TPP), a lipophilic cation, enables its accumulation into the mitochondria of cancer cells more than ~10 times greater than into normal cells as the mitochondrial membrane potentials (~ -220 mV) of cancer cells exhibits more negative charge than that of normal cells (~ -160 mV). The conjugation of TPP with bioactive molecules (e.g. small molecules and peptides) thus would provide a promise approach to target and disrupt the mitochondria of cancer cells, enhancing the efficacy of cancer chemotherapy. Recently, we reported that the supramolecular polymerization of dipeptide inside the mitochondria induced the dysfunction of mitochondria by disrupting the membrane, resulting in the selective apoptosis of cancer cells. Due to the more negative mitochondria membrane potentials in cancer cells compared to normal cells, the TPP-conjugated molecules highly accumulated in the cancer cells and induced the self-assembled structures.

In addition, we describe a mitochondria-targeting biomineralization system that favorably can induce silicification and consequent apoptosis of various cancer cells. The biomineralization system features triphenylphosphonium (TPP) and triethoxysilane (mineralization monomer). The TPP enabled its accumulation into the mitochondria of cancer cells more than 7 times, compared with normal cell. Very intriguingly, the silicification of the triethoxysilane moiety to form biomierals in cancerous mitochondria results in apoptosis thorough mitochondria dysfunction, while there is no toxic effect into normal cell at the same concentration. Furthermore, this system efficiently inhibits the tumor growth of the mouse xenograft cancer model, which is very interesting and efficient anti-cancer therapy with simple molecular design. These results provide a new insight into the use of the mitochondrial targeting molecules for the regulation of cellular functions and a therapeutic approach

Electronic Materials and Photonics Division
Room 101A - Session EM+MI+MN+NS-ThM

Nanostructures for Electronic and Photonic Devices

Moderators: Sang M. Han, University of New Mexico, Jason Kawasaki, University of Wisconsin - Madison

8:00am **EM+MI+MN+NS-ThM1 Extreme Nanophotonics from Ultrathin Metallic Junctions**, ***Maiken Mikkelsen**,* Duke University **INVITED**

New optical nanomaterials hold the potential for breakthroughs in a wide range of areas from ultrafast optoelectronics such as modulators, light sources and hyperspectral detectors, to efficient upconversion for energy applications, bio-sensing and on-chip components for quantum information science; they also serve as inspiration for entirely new devices and technologies. An exciting opportunity to realize such new nanomaterials lies in controlling the local electromagnetic environment on the atomic- and molecular-scale, (~1-10 nm) which enables extreme field enhancements, but represents a largely unexplored length scale. We use creative nanofabrication techniques at the interface between chemistry and physics to realize this new regime, together with advanced, ultrafast optical techniques to probe the emerging phenomena. Here, I will provide an overview of our recent research demonstrating tailored light-matter interactions by leveraging ultra-small plasmonic cavities fabricated using bottom-up techniques. Examples of our demonstrations include perfect absorbers and combinational colors [*Adv. Mat. 27, 7897 (2015)*, *Adv. Mat. 29, 1602971 (2017)*], actively tunable nanostructures [*Nano Lett., 18, 853 (2018)*], tailored emission from two-dimensional semiconductor materials [*Nano Lett. 15, 3578 (2015)*, *ACS Phot. 5, 552 (2018)*] and strong coupling.

8:40am **EM+MI+MN+NS-ThM3 The Geode Process: A Route to the Large-Scale Manufacturing of Functionally-Encoded Semiconductor Nanostructures**, *M. Mujica, G. Tutuncuoglu, V. Breedveld, S.H. Behrens,* ***Michael Filler**,* Georgia Institute of Technology

Future large-area electronic and photonic technologies will require the manufacturing of materials and devices at very high rates without sacrificing nanoscale control of structure and composition. Semiconductor nanowires, for example, can be produced with exquisite spatial control of composition and morphology using the vapor-liquid-solid (VLS) mechanism that, however, remains limited to very small manufacturing rates. Here, we introduce the Geode process to synthesize functionally-encoded semiconductor nanowires at throughputs orders of magnitude beyond the state-of-the-art. Central to the Geode process are sacrificial, porous-walled, seed particle-lined silica microcapsules, whose interior surface serves as a high-surface area growth substrate. Microcapsules protect the growing nanostructures, are produced with a scalable emulsion templating technique, and are compatible with large-scale chemical reactors. We will show how microcapsule structure and drying is influenced by silica nanoparticle type and concentration, emulsification parameters, and nanoparticle cross-linking agent. We will also demonstrate the synthesis of Si nanowires with programmable dopant profiles on the microcapsule interior, which not only shows the versatility of the process, but also allows the impact of precursor gas transport limitations to be characterized.

9:00am **EM+MI+MN+NS-ThM4 Disordered Microsphere-Based Coatings for Effective Radiative Cooling under Direct Sunlight**, *S. Atiganyanun, J. Plumley, K. Hsu,* University of New Mexico*; T.L. Peng,* Air Force Research Laboratory*;* ***Sang M. Han**, S.E. Han,* University of New Mexico

Radiative cooling is a process where a material loses heat due to strong emission of photons in the mid-infrared spectrum and enhanced light scattering in the solar region. This process would allow cooling of materials below the ambient temperature under the sun without the use of electricity and therefore would significantly reduce energy consumption. In this work, we have demonstrated a passive radiative cooling of disordered silica microsphere coatings below the ambient temperature while exposed to direct sunlight. To fabricate the coatings, silica microspheres are deposited by colloidal sedimentation method and spray coating method. In the first method, silica colloidal stability is disrupted by addition of KCl solution. The instability causes the colloids to agglomerate and sediment, creating a disordered uniform coating. In the second method, much like commercial painting, the colloidal solution is forced through a spray nozzle and deposited onto a substrate. Scanning electron microscopy show that the resulting structures are disordered without short- or long-range order. Optical measurements also indicate that the coatings produced under optimal conditions have a short transport photon mean free path of approximately 4-8 µm in the solar spectral region. These coatings also exhibit high emissivity above 95% in the atmospheric transparency window. These results suggest strong photon scattering properties in the visible region, while providing a strong thermal emission. Such films would enable effective radiative cooling. To test the cooling performance, we apply this film on top of a black substrate and expose the material to a direct sunlight during the summer in New Mexico. Temperature measurement of the samples shows that our coating reduces the substrate temperature below that of the ambient air by as much as 12 °C during daytime. Similar testing with a commercial solar-rejection paint indicates that the silica coating performs better than the commercial paint by 4.7 °C on average. Additionally the similar technique is used to fabricate disordered coatings made of polystyrene-polymethyl methacrylate microspheres. Outdoor experiments have shown that the polymer coatings perform better than the commercial paint by 5.5 °C on average. Disordered coatings made of microspheres in a paint format will also be discussed.

9:20am **EM+MI+MN+NS-ThM5 Assessing Strain Relaxation in Nanostructured InGaN Multiple Quantum Wells Using X-Ray Diffraction Reciprocal Space Mapping and Photoluminescence Spectroscopy***, **Ryan Ley**, C.D. Pynn, M. Wong, S.P. DenBaars, M.J. Gordon,* University of California at Santa Barbara

The III-Nitrides are excellent materials for LEDs, lasers and power electronics due to their tunable bandgap and high defect tolerance. These materials are increasingly important for displays in mobile and portable electronic devices, which currently suffer from short battery lives because displays based on liquid crystals or organic LEDs are inefficient. Producing high quality III-Nitride material with the indium compositions needed for efficient green and red emission is presently very challenging, due in large part to strain effects resulting from the large lattice mismatch between InGaN and GaN. However, there are some indications that nanostructuring can reduce or eliminate some of these strain issues.

This talk will highlight our recent work using colloidal and templated lithography and Cl2 /N2 plasma etching to fabricate nanoscale InGaN/GaN LED structures (diameter = 150-600nm), and how sub micron scale patterning affects the strain state and optical behavior of MQW emitters. InGaN/GaN LED structures were grown by MOCVD on c-plane sapphire substrates and characterized before and after nanopatterning using on-axis (0002) and off-axis (10-15 and 11-24) XRD reciprocal space maps (RSM), rocking curves and photoluminescence (PL) spectroscopy at 14K. RSM analysis found degrees of relaxation of 30% and 20% for the smallest and largest structures, respectively, and rocking curves revealed a 0.7nm decrease in the InGaN quantum well thickness. These relaxation effects also correlate well with spectral blue shifts (~10-15nm) in the PL, which are supported by 1D quantum mechanical and electrostatic simulations. Overall, this work shows that nanopatterning of InGaN/GaN active emitters at sub-micron length scales can reduce strain related issues in the III-Nitrides and potentially allow higher incorporation of indium for green and red emission.

9:40am **EM+MI+MN+NS-ThM6 Scalable, Tunable, and Polarization-Independent High Contrast Grating Reflectors for Integration into Resonant-Cavity micro-LEDs***, **Pavel Shapturenka**, S.P. DenBaars, M.J. Gordon,* University of California at Santa Barbara

III-nitride blue and green micro-LEDs have exhibited quantum efficiencies of over 40%, which is a nearly fivefold efficiency boost over current OLED and LCD digital display technologies. In order to realistically continue LED miniaturization below 10 microns for high-resolution and near-eye pixel displays, it is necessary to maintain emission directionality and output power. One method to accomplish this is to make a resonant-cavity micro-LED device with a high-reflectance mirror and an output coupler.

We demonstrate a low-cost, tunable, and scalable colloidal lithography method to fabricate suspended TiO_2 high-contrast grating (HCG) reflectors across the visible wavelength range for eventual integration as an output coupler in a resonant-cavity LED. Silica spheres (310-960 nm diameter), deposited via Langmuir-Blodgett dip-coating, were used as a mask to define a quasi-ordered, hexagonal pattern on a 200 nm thick TiO_2 film. Subsequent pattern transfer with SF_6 reactive ion and XeF_2 chemical etching of sacrificial Si layers beneath the TiO_2 layer yielded a periodic, high index contrast between the suspended array structure and the surrounding air medium. Near-normal-incidence reflectance measurements on structures of increasing hole pitch (310-960 nm) showed an increase in maximum reflected wavelength from 370 to >1000 nm, while maintaining a high-%R bandwidth of 40-100 nm. The reflectance was also observed to be polarization-independent. Finite-difference time domain (FDTD) simulations of structural imperfection stemming from the colloidal lithography process, e.g., deviations in hole diameter, pitch, and hexagonal symmetry, indicate that absolute reflectance is most affected by hole offset from hexagonal lattice positions. The talk will highlight processing methods, optical characterization of HCGs, and underlying trends in the effect of HCG geometry on optical response as predicted by FDTD simulations. This work suggests that scalable fabrication of visible-wavelength HCGs is feasible and holds promise for integration into resonant-cavity LEDs.

11:00am **EM+MI+MN+NS-ThM10 Nano-optical Activation of Defect-bound Excitons in Monolayer WSe_2: Towards Room-temperature 2D Single-photon Optoelectronics***, **Jim Schuck**,* Columbia University **INVITED**

The emergence of two-dimensional (2D) monolayer transition metal dichalcogenides (1L-TMDC) as direct bandgap semiconductors has rapidly accelerated the advancement of room temperature, 2D optoelectronic devices. Optical excitations on the TMDCs manifest from a hierarchy of electrically tunable, Coulombic free-carrier and excitonic many-body phenomena. In our most recent nano-optical investigations of these materials, we have demonstrated that a model hybrid architecture, a nano-optical antenna and a 1L-WSe_2 nanobubble, activates the optical activity of BX states at room temperature and under ambient conditions. These results show that engineered bound-exciton functionality as, in this case, localized nanoscale light sources, can be enabled by an architectural motif that combines localized strain and a nano-optical antenna, laying out a possible path for realizing room-temperature single-photon sources in high-quality 2D semiconductors.

11:40am **EM+MI+MN+NS-ThM12 Light Scattering Properties of Silver Nanoprisms in Different Environments***, **Yuri Strzhemechny**,* Texas Christian University*; S. Requena,* Harris Night Vision*; H. Doan,* Texas Christian University*; S. Raut,* University of North Texas Health Science Center*; Z. Gryczynski,* Texas Christian University*; I. Gryczynski,* University of North Texas Health Science Center

Embedding nanostructures into different environments, such as polymer matrices, organic and biological solutions oftentimes produces unique optoelectronic properties of the resulting compound system that are distinct from those of the host and nano-filler. Such strong modifications can be caused by the interface phenomena, the change in the spatial distribution and orientation of the nanostructures or a combination thereof. In this work, we report on optical properties of silver triangular prism nanoparticles embedded in water, lipid solutions, and polyvinyl alcohol (PVA) polymer thin films. For our studies, using a common chemical reduction routine, we synthesized, batches of silver nanoparticles with different size distributions and distinct size-dependent dipole resonance spectra. Silver nanoprisms suspended in water yielded a noticeable wavelength-dependent depolarization of scattered light associated with different surface plasmon modes. Consequently, the same nanostructures were placed into lipid environments to estimate the rejection of a polarized background scattering during depolarization measurements. After that, the composite thin films were fabricated via incorporation of silver nanoparticles into PVA. We studied linear dichroism in those Ag/PVA films, as-prepared and subjected to controllable stretching. Re-orientation of the nanoprisms upon stretching leads to a significant increase of the linear dichroism for the plasmonic modes associated with the in-plane dipole oscillations and a decrease of the linear dichroism corresponding to the out-of-plane plasmonic modes. These observations are in good agreement with the assumption that stretching of the nanocomposite films leads to an anisotropic realignment of the nanoprisms.

12:00pm **EM+MI+MN+NS-ThM13 Core-Shell Processing of BTO Nanocomposites for Optimal Dielectric Properties***, **Kimberly Cook-Chennault**,* Rutgers University

High permittivity polymer-ceramic nanocomposite dielectric films leverage the ease of flexibility and processing of polymers and functional properties of ceramic fillers. Physical characteristics of these materials can be tuned for application to a variety of applications, such as, advanced embedded energy storage devices for printed wired electrical boards and battery seperators. In some cases, the incompatibility of the two constituent materials; hydrophilic ceramic filler and hydrophobic epoxy can limit the filler concentration and therefore, dielectric properties of these materials. Use of surfactants and core-shell processing of composite fillers is traditionally used to achieve electrostatic and steric stabilization for adequate ceramic particle distribution. This work aims to understand the role of surfactant concentration in establishing meaningful interfacial layers between the epoxy and ceramic filler particles by observing particle surface morphology, dielectric permittivity and device dissipation factors. A comprehensive study of nanocomposites that were comprised of non-treated and surface treated barium titanate (BT) embedded within an epoxy matrix was performed. The surface treatments were performed with ethanol and 3-glycidyloxypropyltrimethoxysilan, where the best distribution, highest value of permittivity (~ 48.03) and the lowest value of loss (~0.136) were observed for the samples that were fabricated using 0.5 volume fraction of BaTiO3 and 0.02 volume fraction of silane coupling agent.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 201A - Session HC+SS-ThM

In-situ Analysis of Heterogeneously Catalyzed Reactions

Moderator: Sharani Roy, University of Tennessee Knoxville

8:00am **HC+SS-ThM1 Structural Characterization of ZnO on Cu(111) by using STM and XPS: Role of Cu-ZnO Interface in Methanol Synthesis***, **Mausumi Mahapatra,** J.A. Rodriguez,* Brookhaven National Laboratory

The ZnO–copper interface plays an important role in the synthesis of methanol from the hydrogenation of (CO_2+ $4H_2$--> CH_3OH + $2H_2O$). The deposition of nanoparticles of ZnO on Cu(111), θ_{oxi} < 0.3 monolayer, create a stable and highly active interface between ZnO and Cu. The ZnO-copper catalysts may be prepared by two different methods: 1) Zn vapor deposited on Cu(111) at ~600 K in an oxygen ambient (reactive vapor deposition), 2) Zn vapor deposited on Cu(111) at 300 K following by heating the surface with oxygen to 600 K (oxidation of surface alloy). The reactivity and stability of the catalysts prepared by the above two methods were tested under CO_2 hydrogenation reaction conditions in a reactor and by using AP-XPS: 1) The ZnO-copper catalyst prepared by method 1 was stable whereas that prepared by method 2 was not stable at the elevated temperatures (500–600 K) used for the CO_2 hydrogenation. The temperature dependent growth and the structural characterization of the ZnO/Cu(111) catalyst, θ_{oxi} < 0.3 monolayer was explored by using STM. Our results show that the size and shape of the ZnO nanoparticles are dependent on the growth temperature. The ZnO/Cu(111) surface prepared by reactive vapor deposition at 450-600 K results in large ZnO triangular islands. However the surface oxidation of a Zn/Cu(111) alloy resulted in very small ZnO clusters.

8:20am **HC+SS-ThM2 Dissociative Adsorption of CO_2 on Cu-surfaces***, **Benjamin Hagman,*** Lund University, Sweden*; A. Posada-Borbón, A. Schaefer,* Chalmers University of Technology, Gothenburg, Sweden*; C. Zhang,* Lund University, Sweden*; M. Shipilin,* Stockholm University, Sweden*; N.M. Martin,* Chalmers University of Technology, Gothenburg, Sweden*; E. Lundgren,* Lund University, Sweden*; H. Grönbeck,* Chalmers University of Technology, Gothenburg, Sweden*; J. Gustafson,* Lund University, Sweden

Due to the urgent problem of global warming, there is a need to reduce the release of the greenhouse gas CO_2 into the atmosphere. A potential approach to limit the CO_2 release is to convert it into useful chemical products, such as methanol [1]. However, the recycling of CO_2 is a challenging task as the molecule is rather inert, which makes it difficult to activate for reduction and subsequent hydrogeneration. The most used metal for this activation is Cu, and a fundamental understanding of how CO_2 interacts with Cu surfaces would promote the development of new catalysts for the reduction of CO_2 [2].

We have studied the CO_2 interaction with both Cu(100) and stepped Cu(911) surfaces at elevated CO_2 pressures using Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS). APXPS gives us the ability to probe the changes of the surface during the chemical reaction. In our case, we see that CO_2 chemisorbs on the surface and dissociates to O and CO, of which CO desorb, while the atomic oxygen remains on the surface.

For the Cu(100) surface, we observe that the rate of oxygen uptake from CO_2 dissociation is constant until the atomic oxygen coverage approaches 0.25 ML, where the rate decreases. After 0.25 ML the rate remains constant until a saturation appears as the oxygen coverage approaches 0.5 ML. Density Functional Theory (DFT) calculations indicate that CO_2 can adsorb and dissociate on both the terraces and steps on Cu(100), however, the dissociation is expected to take place mainly on the step as the barrier for the dissociation is lower at such sites. The atomic oxygen, from the dissociation at the step, is expected to diffuse away from the step to the terrace, leaving the number of active sites constant, and explaining the constant oxygen uptake rate. Both the experiment and DFT calculations indicate that the atomic oxygen from the dissociation of CO_2 poisons the adsorption and dissociation of CO_2 at an oxygen coverage above 0.25 ML, however, we believe that the step can remain active after 0.25 ML.

To confirm the role of the steps on Cu(100), we have also studied the interaction of CO_2 and Cu(911). We observe the CO_2 adsorption is significantly facilitated by the presence of the steps on the Cu(911) surface as compared to the flat Cu(100). The effect of the facilitated CO_2 adsorption on the subsequent dissociation will be discussed.

References:

[1] W. Wang, et al., Chem. Soc. Rev., **40** (2011), pp. 3703-3727

[2] M. D. Porosoff, et al., Energy Environ. Sci., **9** (2016), pp. 62-73.

8:40am **HC+SS-ThM3 Infrared Spectroscopy of Carbon Dioxide Hydrogenation over the Cu(111) Surface Under Ambient Pressure Conditions***, C.M. Kruppe,* ***Michael Trenary,*** University of Illinois at Chicago

Copper catalysts are used in the water gas shift reaction to convert mixtures of carbon monoxide and water to hydrogen and carbon dioxide. Conversely, the reverse water gas shift reaction utilizes carbon dioxide as a resource. Related to the reverse water gas shift reaction is the synthesis of methanol from carbon dioxide and hydrogen. The mechanisms of these reactions involve several possible surface intermediates, each of which should be identifiable by their vibrational spectra. We have used reflection absorption infrared spectroscopy (RAIRS) to study these reactions under ambient pressures in the range of 0.1 to 150 Torr. In the presence of 150 Torr of carbon dioxide, a peak is observed at 1294 cm^{-1}, which is assigned to the symmetric stretch of an adsorbed CO_2 molecule that is bent through its interaction with the surface. Upon addition of 150 Torr of $H_2(g)$ at 300 K, the 1294 cm^{-1} peak of CO_2 is greatly diminished, while new peaks appear due to gas phase water. By performing the experiment with polarized infrared radiation, the gas phase and surface species are easily distinguished. When the Cu(111) surface is annealed to higher temperatures, numerous changes occur in the spectra revealing the formation of a series of surface intermediates containing C–H bonds, including methoxy, OCH_3. The results demonstrate that CO_2 hydrogenation is readily achieved over a Cu(111) model catalyst and that surface intermediates can be easily detected with RAIRS.

9:00am **HC+SS-ThM4 Oxide Formation on Ir(100) Studied by in-Situ Surface X-ray-Diffraction***, **Stefano Albertin**, U. Hejral,* Lund University, Sweden*; R. Felici,* SPIN-CNR, Italy*; R. Martin,* University of Florida*; M. Jankowski,* ESRF, France*; J.F. Weaver,* University of Florida*; E. Lundgren,* Lund University, Sweden

Methane (CH_4) conversion into higher added value hydrocarbons is done through a number of complex catalytic steps, and has been studied for many years [1]. The initial and often rate limiting step in the reaction is the dissociation of the molecule on the metal catalyst surface. Because alkane C–H bonds are among the least reactive known, no process for direct conversion of CH_4 into methanol (CH_3OH) has so far been developed.

IrO_2(1 10) surface grown on Ir(100) has shown facile dissociation of CH_4 at liquid nitrogen temperatures [2], as well as oxidizing H_2 to -OH [3]: two steps that could have importance for the development of a new direct methane-to-methanol catalysts.

In this contribution we will present recent results from in-situ Surface X-ray Diffraction (SXRD) recorded at beamline ID03 at the ESRF from the oxidation of a Ir(100) surface. We find that the Ir(100) surface oxidizes into a bulk oxide at a temperature of 775 K and a pressure of 5 mbar of O_2 similar to what observed in [2], forming a predominantly rutile IrO_2(110) oriented surface. Our study also demonstrates that lowering the partial O_2 pressure or the temperature results in the formation of a number of different Ir sub-oxides similar to the ones found for Ir(111) [4], and the structures formed will be discussed in this contribution.

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9:20am **HC+SS-ThM5 Dynamic Nanocatalysts: Environmental Effects***, **Beatriz Roldan Cuenya**,* Fritz-Haber Institute of the Max Planck Society **INVITED**

In order to comprehend the catalytic performance of metal nanostructures, their dynamic nature and response to the environment must be taken into consideration. The working state of a nanocatalyst might not be the state in which the catalyst was prepared, but a structural and/or chemical isomer that adapted to the particular reaction conditions. Furthermore, deactivation phenomena taking place under reaction conditions can only be understood, and ultimately prevented, if sufficient information is available on the catalyst morphology, structure, chemical state, and surface composition while at work.

I will first describe novel approaches for the synthesis of size- and shape-controlled nanoparticles and nanostructured metallic films (e.g. Au, Cu, Ag, Zn, CuZn, CuCo, CuNi, AgSn, NiGa) and their functionalization/activation based on plasma treatments. Subsequently, I will illustrate how to follow the evolution of their morphology and surface composition under different gaseous and liquid chemical environments in the course of a catalytic reaction. This will be implemented using a synergistic combination of *in situ* and *operando* microscopy (EC-AFM, STM, TEM) and spectroscopy (XAFS, AP-XPS) methods. It will be highlighted that for structure-sensitive reactions, catalytic activity, selectivity, and stability can be tuned through controlled synthesis. Examples of catalytic processes which will be discussed include the gas- and liquid-phase oxidation of 2-propanol and the gas-phase hydrogenation and electrochemical reduction of CO_2. Emphasis will be given to elucidating the role of the size, shape, composition, chemical state, surface defects and roughness of the catalysts in the activity and selectivity of the former reactions.

11:00am **HC+SS-ThM10 Atomic Layer Deposition (ALD) Synthesis of Au/TiO_2/SBA-15 Catalysts***, W. Ke, X. Qin, **Francisco Zaera**,* University of California, Riverside

Au/Titania catalysts have received much attention in recent years because of their ability to promote photocatalytic water splitting as well as selective low-temperature oxidation reactions. The uniqueness of these catalysts is ascribed to both the nanometer-size of the gold nanoparticles and the reducibility of the titania support. Here we report results from studies on the use of ALD to control the titania film thickness, to tune its degree of reducibility and explore the role of that reducibility in catalysis. SBA-15, a mesoporous solid with well-defined pore structure, was used as the base material in order to be better able to characterize the deposited titania films. Surface reducibility was tested as a function of film thickness by CO infrared-absorption spectroscopy titrations and by EPR, and the catalytic performance via kinetic measurements for CO oxidation. Unique trends were observed at intermediate (2-4 ALD cycles) film thicknesses.

11:20am **HC+SS-ThM11 Enhanced Stability of Pt/Cu Single-Atom Alloy Catalysts: In Situ Characterization of the Pt/Cu(111) Surface in an Ambient Pressure of CO***, **Juan Pablo Simonovis Santamaria**,* Brookhaven National Laboratory

Research in catalysis has steered towards the design and synthesis of more efficient catalysts that can yield better quality products at lower costs. In this regard, bimetallic alloys where the active metal is mono-atomically dispersed have shown unique activity, selectivity and stability compared to their monometallic counterparts. These so called single atom alloys (SAA) are of interest since small amounts of active metals can be used reducing catalysts cost. However, the chemical interactions between active site and reacting molecules are still poorly understood, thus careful characterization of these moieties under reaction conditions is needed to elucidate fundamental reaction steps that can clarify the role of the active site during the catalytic process.

In this study, we used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) performed at the 23-ID-2 (IOS) beamline at the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory to compare the stability of Pt/Cu(111) SAA in ultrahigh vacuum (UHV) and ambient pressure conditions, particularly how its surface structure and composition can be influenced by the presence of a reactant gas such as CO. Because of the surface and chemical sensitivities of AP-XPS, we can directly probe the Pt atoms to clearly identify surface/subsurface layers of the metal and monitor its evolution under different experimental conditions.

Our study showed that the Pt (0.05 ML)/ Cu(111) SAA is thermally unstable above 400 K under UHV conditions, since higher temperatures cause Pt on the surface to migrate to the subsurface and, eventually, to the bulk. This metal diffusion into the subsurface could lead to the deactivation of a potential catalyst. However, under ambient pressures of CO, the surface and subsurface Pt are thermally stable up to 500 K, resisting diffusion into the bulk. In fact, thermal treatment in CO of a sample that was previously heated under UHV conditions lead to the recovery of Pt that had diffused to the subsurface, suggesting that, within 300-500 K the diffusion process is reversible to some extent. However, this thermal stability as well as surface recovery in CO comes at the expense of slightly enhanced CO−Pt interactions likely caused by the presence of neighboring subsurface Pt resulting from the thermal-induced restructuring of the subsurface layer. Whether the post-heated surface still resists the poisoning effects of CO remains to be seen, but these results demonstrate the importance of studying not only the changes in the surface of a catalyst under reaction conditions but also the near-surface region, which may also influence the reactivity of the catalyst.

11:40am **HC+SS-ThM12 Multiscale Modelling of Metal Oxide Interfaces and Nanoparticles***, **Kersti Hermansson**, P. Mitev, J. Kullgren, P. Broqvist,* Dept of Chemistry-Ångström, Uppsala University, Sweden **INVITED**

Redox-active metal oxide surfaces and interfaces – such as electrodes, catalysts, and sensors – play crucial roles in our society and in the development of new materials and greener technologies. In the scientific literature, a full arsenal of experimental methods are being used to help characterize such interfaces. At the same time, the number of theoretical studies in the literature steadily increases, providing mechanistic information at a detail that is hard to beat by experiment. *Are such theoretical results accurate enough*?

I will describe some of our efforts to develop multiscale modelling protocols for metal oxide surfaces and nanoparticles (e.g. of CeO_2, ZnO and MgO). We combine a range of theoretical methods including ***DFT, tight-binding-DFT*** [1]***, and reactive force-field models*** A key question is whether it is really possible to model redox-active metal oxides *without including the electrons*?

The O_2 chemistry of reducible oxides is rich and famous and I will therefore also discuss various aspects of how adsorbed oxygen on nanoparticles and clusters can stabilize in the form ***superoxide ions*** (O_2^-) and the implications that this may have on their reactivities. Microkinetic modelling results to mimic experimental TPD spectra will be presented as well as mechanistic detail that is currently only possible to obtain from modelling.

The H_2O molecule deserves special attention as ***hydroxylation/hydration*** changes the properties and reactivities of metal oxides, often with far-reaching consequences. We recently studied a thick water film on a ZnO(10-10) surface using MD simulations from a neural-network-generated potential landscape of DFT quality combined with anharmonic vibrational frequency calculations.[2] and were able to relate H-bond structure and frequencies in a meaningful way. In an attempt to reach a step further in terms of understanding found that a ***parabola-like 'OH frequency vs. in-situ electric field' relation*** holds for both intact and dissociated water molecules on ionic surfaces [3], and for both thin and thick films (unpublished).

I will also inform about the European Materials Modelling Council (https://emmc.info/), which aims to promote the use of materials modelling in –not least– industry.

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Advanced Ion Microscopy Focus Topic
Room 203B - Session HI+AS-ThM

Advanced Ion Microscopy & Surface Analysis

Moderators: Gregor Hlawacek, Helmholtz Zentrum Dresden-Rossendorf, Germany, Shida Tan, Intel Corporation

8:00am **HI+AS-ThM1 Pushing the Limits: Secondary Ion Mass Spectrometry with Helium Ion Microscopy***, **Alex Belianinov**,* Oak Ridge National Laboratory*; S. Kim,* Pusan National University, South Korea*; M. Lorenz,* University of Tennessee Knoxville*; A.V. Ievlev, A. Trofimov, O.S. Ovchinnikova,* Oak Ridge National Laboratory **INVITED**

Material functionality is defined by structure and chemistry often at micro- and nano-scale. The effects are coupled; however, few methods exist that can simultaneously map both. This presents a challenge for material scientists. Functional materials are continuously increasing in complexity, and the number of studies devoted to designing new materials often overwhelms characterization capacity. Recently, attention has been devoted to offer hardware and software solutions in chemical imaging, where a blend of *in-situ* and *ex-situ* techniques are used to capture and describe material behavior using combinatorial data. However, many of the emerging techniques need to be carefully validated and contrasted against existing approaches.

This talk will cover the performance of the recently developed combinatorial Helium Ion Microscopy (HIM) and Secondary Ion Mass Spectrometry (SIMS) tool on a wide variety of conductive and insulating samples. While the HIM imaging and milling performance to explore the physical structure has been repeatedly demonstrated, questions on the effect, quality, and resolution of a Neon beam SIMS remain. Ion yields, chemical resolution, and charge compensation results and strategies will be presented and discussed.

Acknowledgement

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

8:40am **HI+AS-ThM3 When HIM meets SIMS***, Tom Wirtz,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; O. De Castro, J. Lovric,* Luxembourg Institute of Science and Technology (LIST)*; J.-N. Audinot,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

In 2015, we first presented a Secondary Ion Mass Spectrometry (SIMS) system which we specifically developed for the Zeiss ORION NanoFab Helium Ion Microscope (HIM) [1]. This SIMS system is based on (i) specifically designed secondary ion extraction optics coupled with post-acceleration transfer optics, providing maximized extraction efficiency while keeping a finely focussed primary ion beam for highest lateral resolution, (ii) a compact floating double focusing magnetic sector mass spectrometer allowing operation in the DC mode at full transmission (and hence avoiding duty cycles like in TOF systems that either lead to very long acquisition times or, for a same acquisition time, intrinsically limit the sensitivity) and (iii) a specific detection system allowing the detection of several masses in parallel. We have demonstrated that our instrument is capable of producing (i) mass spectra with high mass resolution, (ii) very local depth profiles and (iii) elemental SIMS maps with lateral resolutions down to 12 nm [1-5]. Furthermore, HIM-SIMS opens the way for in-situ correlative imaging combining high resolution SE images with elemental and isotopic ratio maps from SIMS [2,3,6]. This approach allows SE images of exactly the same zone analysed with SIMS to be acquired easily and rapidly, followed by a fusion between the SE and SIMS data sets [6]. Moreover, thanks to its depth profiling capability of the SIMS add-on, it is now possible to follow the chemical composition in real time during nano-patterning in the HIM for applications such as end-pointing.

Here, we will review the instrument performance and present a number of examples taken from various fields of applications, with a special emphasis on 3D reconstructions in materials science (battery materials, solar cells, micro-electronics) and on correlative HIM-SIMS bioimaging.

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9:00am **HI+AS-ThM4 Deciphering Chemical Nature of Ferroelastic Twin Domain in $MAPbI_3$ perovskite by Helium Ion Microscopy Secondary Ion Mass Spectrometry***, Yongtao Liu,* University of Tennessee*; L. Collins,* Oak Ridge National Laboratory*; R. Proksch,* Asylum Research an Oxford Instruments Company*; S. Kim,* Oak Ridge National Laboratory*; B.R. Watson,* University of Tennessee*; B.L. Doughty,* Oak Ridge National Laboratory*; T.R. Calhoun, M. Ahmadi,* University of Tennessee*; A.V. Ievlev, S. Jesse, S. Retterer, A. Belianinov, K. Xiao, J. Huang, B.G. Sumpter, S.V. Kalinin,* Oak Ridge National Laboratory*; B.H. Hu,* University of Tennessee*; O.S. Ovchinnikova,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Hybrid organic-inorganic perovskites (HOIPs) have recently attracted attention due to its success in optoelectronics, largely due to power conversion efficiency, which has exceeded 20% in a short time. Recently, the appearance of twin domains in $MAPbI_3$ has been described ambiguously in a number of investigations. While all previous publications are limited in the descriptions of ferroelectric and/or ferroelastic nature, given (i) the correlation of defect chemistry and ferroelasticity, (ii) the coupling of ferroelectricity and ionic states, the chemistry of this twin domain can no longer be ignored. In earlier investigations, the twin domain size is revealed in the range of 100 nm- 400 nm, well in the detectability of helium ion microscopy secondary ion mass spectrometry (HIM-SIMS) (spatial resolution ~10 nm). Therefore, in this work, we correlate HIM-SIMS with multiple image techniques to unveil the chemical nature of the twin domain in $MAPbI_3$ perovskite.

Our scanning probe microscopy (SPM) studies indicate the variation of elasticity and energy dissipation between domains. Moreover, correlating SPM with scanning electron microscope (SEM), we observed smooth topography and twin domain contrast in SEM image, simultaneously, indicating the twinning contrast in SEM image is not due to morphology. These results allow us to suppose the chemical variation between twin domains, suggesting the need of clarifying the chemical difference between domains.

Using HIM-SIMS, which combines high-resolution imaging <0.25 nm of helium ion microscopy with the chemical sensitivity of secondary ion mass spectrometry (SIMS), we can detect ion distribution with a spatial resolution of 10 nm, allowing us to quantitatively explore the chemical composition of the twin domains (100 nm-400 nm). A HIM-SIMS using two gas field ionization sources (He^+ and Ne^+) was utilized for mass-selected chemical imaging of perovskite samples as well as identification of chemical species by spectrum collection in this study. In a positive mode measurement, $CH_3NH_3^+$ (m/z~32) chemical map shows that the $CH_3NH_3^+$concentration differs both in grains and twin domains, however, the Pb^+ (m/z~208) distributes uniformly. These results clarify that the chemical variation between domains originates from $CH_3NH_3^+$ segregation. For the most relevant for the optoelectronic applications of HOIPs, we have shown that this chemical variation affects HOIPs' interaction with light. Combining HIM-SIMS with multiple image techniques, this work offers insight into the fundamental behaviors of the twin domain in $MAPbI_3$, as well as a new line of investigative thought in these fascinating materials.

9:20am **HI+AS-ThM5 Helium and Neon Ion Microscopy for Microbiological Applications***, Ilari Maasilta,* University of Jyvaskyla, Finland **INVITED**

Imaging of microbial interactions has until now been based on well-established electron microscopy methods. In this talk I review our recent drive to study microbiological samples using a helium ion microscopy (HIM). The main focus will be given on bacterial colonies and interactions between bacteria and their viruses, bacteriophages, which we imaged in situ on agar plates [1]. Other recent biological applications will also be briefly discussed. In biological imaging, HIM has advantages over traditional scanning electron microscopy with its sub-nanometer resolution, increased surface sensitivity, and the possibility to image nonconductive samples. Furthermore, by controlling the He beam dose or by using heavier Ne ions, the HIM instrument provides the possibility to mill out material in the samples, allowing for subsurface imaging and in situ sectioning.

Here, we present the first HIM-images of bacterial colonies and phage–bacterium interactions are presented at different stages of the infection as they occur on an agar culture. The feasibility of neon and helium milling is also demonstrated to reveal the subsurface structures of bacterial colonies on agar substrate, and in some cases also structure inside individual bacteria after cross-sectioning. The study concludes that HIM offers great opportunities to advance the studies of microbial imaging, in particular in the area of interaction of viruses with cells, or interaction of cells with biological surfaces.

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11:00am **HI+AS-ThM10 Characterization of Soot Particles by Helium Ion Microscopy**, ***André Beyer***, *D. Emmrich, M. Salamanca, L. Ruwe, H. Vieker, K. Kohse-Höinghaus, A. Gölzhäuser,* Bielefeld University, Germany

Complementary techniques for the characterization of soot particles are needed to gain insight into their formation processes. In this contribution, we focus on Helium Ion Microscopy (HIM) which allows high contrast imaging of soot particles with sizes down to 2 nm. Soot formation was realized with well-defined model flames from different fuel compositions. The particles were sampled on silicon substrates at different positons within the flame which allows choosing the particles degree of maturity. Large numbers of particles were recorded with a single HIM image in a relatively short time. A number of such images were combined to obtain meaningful particle size distributions. In addition, the following geometric properties of soot particles were evaluated: sphericity, circularity, and fractal dimension. Comparison with other experimental techniques as well as theoretical model calculations demonstrate the strength of the HIM characterization method [1-3].

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11:20am **HI+AS-ThM11 Development of a Surface Science Spectra Submission Form for Low Energy Ion Scattering (LEIS)**, *M.R. Linford,* ***Tahereh Gholian Avval,*** Brigham Young University*; H.H. Brongersma, T. Grehl,* IONTOF GmbH, Germany

Historically, Surface Science Spectra (SSS) has been an important archive for X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and time-of-flight secondary ion mass spectrometry (ToF-SIMS) data; this detailed, peer-reviewed database now consists of thousands of submissions and spectra that represent these techniques. Thus, SSS has been and continues to be a valuable resource to the surface community. Recently, SSS has begun to expand the surface/material techniques it covers. For example, it now accepts spectroscopic ellipsometry submissions on the optical properties of materials. It is anticipated that submissions in this area will slowly increase so that SSS will become a valuable source of information in this area as well.

In this presentation we discuss the development of an SSS submission form for low energy ion scattering (LEIS). Fields in the form that will be discussed include the abstract, introduction, data, and conclusions. In an SSS submission, the provenance of the sample is carefully documented. A detailed description is also required of the equipment used and of all of its relevant operating parameters – the nature of its beams, the beam energies, the analyzer geometry, etc. The original data collected by the submitter must be supplied, and representative examples of it must be plotted.

Finally, we will show sample submissions based on this new form that should have been submitted for publication by AVS 2018. These will include LEIS submissions of CaF_2, SrO, and Al_2O_3 reference materials

11:40am **HI+AS-ThM12 Time of Flight Backscatter and Secondary Ion Mass Spectrometry in the Helium Ion Microscope**, ***Nico Klingner***, *R. Heller, G. Hlawacek, J. von Borany, S. Facsko,* Helmholtz Zentrum Dresden-Rossendorf, Germany

Existing Gas Field Ion Source (GFIS) based focused ion beam (FIB) tools suffer from the lack of a well integrated analytic method that can enrich the highly detailed morphological images with materials contrast. While Helium Ion Microscopy (HIM) technology is relatively young several efforts have been made to add such an analytic capability to the technique. So far, ionoluminescence, backscattering spectrometry (BS), and secondary ion mass spectrometry (SIMS) using a magnetic sector or time of flight (TOF) setups have been demonstrated.

After a brief introduction to HIM itself and a summary of the existing approaches I will focus on our own time of flight based analytic approaches. TOF-HIM is enabled by using a fast blanking electronics to chop the primary beam into pulses with a minimal length of only 20 ns. In combination with a multichannel-plate based stop detector this enables TOF backscatter spectrometry (TOF-BS) using He ions at an energy of only 30 keV. The achieved lateral resolution is 54 nm and represents a world record for spatially resolved backscattering spectrometry.

Finally a dedicated extraction optics for positive and negative secondary ions has been designed and tested. The setup can be operated in point and shoot mode to obtain high resolution SIMS data or in imaging mode to obtain lateral resolved maps of the sample surface composition. First experiments revealed a very high relative transmission of up to 76% which is crucial to collect enough signal from nanoparticles prior to their complete removal by ion sputtering. The mass resolution of 200 is sufficient for many life science applications that rely on the isotope identification of light elements (e.g.: C, N). The lateral resolution of 8 nm has been evaluated using the knife edge method and a 75%/25% criterion which represents a world record for spatially resolved secondary ion images.

12:00pm **HI+AS-ThM13 Helium and Neon Focused Ion Beam Hard Mask Lithography on Atomic Layer Deposition Films**, ***Matthew Hunt,*** California Institute of Technology*; J. Yang,* University of Texas at Austin*; S.A. Wood, O.J. Painter,* California Institute of Technology

A hard mask lithography technique has been developed wherein a helium or neon focused ion beam (FIB) is used to directly etch a pattern into a thin, atomic layer deposition (ALD) film before then transferring the pattern into the underlying material using a reactive ion etch (RIE). The technique takes advantage of small He-FIB and Ne-FIB probe sizes, capable of directly etching patterns with feature sizes on the order of 1s and 10s of nanometers, respectively, while sidestepping several negative consequences associated with direct etch, namely that low sputter rates prevent large-area patterning from being carried out efficiently, with straight sidewalls, and/or without inducing substrate swelling. An example of the technique is presented here in which (1) 4-10 nm of ALD aluminum-oxide is applied as the hard mask on a 60 nm thick film of aluminum, (2) a <10 pC/um Ne-FIB dose is used to pattern lines that barely etch through the hard mask, and (3) a $Cl_2/CH_4/H_2$ RIE is used to etch the underlying aluminum in 10s of seconds. Neon FIB writing time is reduced by a factor of 20 or more compared to directly etching through the full 60 nm aluminum film. Nanowires as thin as 25 nm are produced with straight sidewalls on 70 nm pitch. This example is being utilized to make superconducting quantum circuit components, e.g. 4 mm long nanocoil inductors that fit into a (20x20) um^2 area. The technique has potentially wide-ranging nanofabrication applications given its amenability to different ALD/substrate material sets and compatibility with both He- and Ne-FIB.

Magnetic Interfaces and Nanostructures Division
Room 203A - Session MI+2D-ThM

Magnetism at the Nanoscale

Moderator: Hendrik Ohldag, SLAC National Accelerator Laboratory

8:20am **MI+2D-ThM2 Magnetic Competition in $La_{0.7}Sr_{0.3}MnO_3$ Thin Films**, ***Mikel B. Holcomb,*** West Virginia University

$La_{0.7}Sr_{0.3}MnO_3$ is a strongly correlated ferromagnetic system, commonly proposed for many magnetoresistance applications. Utilizing many techniques (bulk magnetometry, neutron reflectometry and resonant x-ray magnetic scattering), we observe magnetic competition between different magnetic phases in many samples under various growth conditions. This competition results in inverted hysteresis loops (common in superparamagnetic nanoparticles) and negative remanent magnetization. While transmission electron microscopy images show pristine epitaxial growth, the data supports that there are regions of different magnetic order. This results in interesting magnetic measurements, that share similarities with ferrimagnets with competing magnetic lattices. Sample growth and optimization were supported by NSF (DMR-1608656), national facility measurements and theory were supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0016176, and optical measurements by American Chemical Society (PRF #56642-ND10). **We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work.**

8:40am **MI+2D-ThM3 Ferromagnetism in 2D Materials**, ***Jiabao Yi,*** The University of New South Wales, Australia **INVITED**

Discovery of graphene has attracted wide interest of research in the family of 2D layered materials including TMDC (transition metal dichalcogenide), silicene, metal oxide and boron nitride. 2D materials have shown many extraordinary properties, such as high carrier mobility, extra-large mechanical strength and high thermal conductivity and excellent performance in energy storages. Due to its two-dimension nature and high carrier mobility, 2D materials are also very promising for spintronics devices. Graphene has shown long spin diffusion length and high spin injection efficiency [1]. Therefore, introducing magnetism into 2D materials becomes one of the research interests in 2D materials. Doping magnetic element into 2D materials is one of the effective methods to achieve magnetism. Most of the research focuses on theoretical calculations. In this presentation, I will introduce both theoretical calculations and experimental results on magnetic element doped 2D materials. From first principles calculations, it shows defects or defect complexes play important role in the magnetism [2]. In addition, ferromagnetism can be tuned by strain [3]. Experimentally, we observe room temperature ferromagnetism in magnetic element doped 2D materials. Especially, giant coercivity and extremely high magnetization have been observed in magnetic element doped MoS_2. Defects and shape anisotropy play critical roles in the high magnetization and coercivity [4,5].

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9:20am **MI+2D-ThM5 New Insights into Nanomagnetism by Low-temperature Spin-polarized Scanning Tunneling Microscopy*, Dirk Sander,*** Max Planck Institute of Microstructure Physics, Germany **INVITED**

Spin-polarized scanning tunneling microscopy at low temperature (8 K) and in high magnetic fields (6 T) is a powerful technique to investigate magnetic properties of individual nanoscale objects ranging in size form single atoms to several thousand atoms [1]. I focus on the magnetization reversal [2] and the spin-dependent electronic properties of bilayer Co [3], Fe-decorated Co and Fe islands on Cu(111). We find a novel noncollinear, helical magnetic order in the Fe islands, which is identified by a magnetic stripe contrast with a period of 1.28 nm [4,5] in bilayer islands. The periodicity increases to 2.2 nm in three-layer thick Fe islands [6]. The high spatial resolution of the spin-polarized scanning tunneling spectroscopy in combination with theory reveals the significance of structural and electronic relaxation [7] for the magnetic anisotropy, for subtle balances between ferromagnetic and antiferromagnetic exchange interaction, and for spin-dependent transport properties [8] of individual, single nanostructures.

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11:00am **MI+2D-ThM10 Materials Optimization to Form Skyrmion and Skyrmion Lattices*, Eric Fullerton,*** University of California at San Diego **INVITED**

There is increasing interest in materials systems where magnetic skyrmions can be observed. I will discuss two materials systems where we observe chiral spin structures at room temperature. The first system is ferrimagnetic Fe/Gd-based multilayers where we observe sub-100-nm skyrmions and skyrmion lattices. However, the chirality of the skyrmions are random indicating they are dipole stabilized (similar to of bubble memory in the 1970's) as opposed to by DMI that favors a fixed chirality. This further allows the formation of bi-skyrmions which result from the merging of two skyrmions of opposite chirality and anti-skyrmions. We find that there is a transition from stripe domains to a skyrmion lattice and then individual skyrmions with magnetic fields and this behavior is sensitive to alloy composition, film thickness, temperature, and field history and only emerges in a narrow range of parameters. Using micromagnetic modeling we are able to quantitatively reproduce our experimental observations. The modeling suggests that the domain wall is Bloch-like in the center of the films but broadens and transitions to more Néel-like towards the surface forming closure domains. The Bloch-like centers have an equal population of the two helicities while the Néel-like part of the walls will have the same helicity at the top of the film and the opposite helicity at the bottom of the film which allows coupling to spin-orbit-torque layers. The second system is Pt/Co(1.1 nm)/Os(0.2 nm)/Pt heterostructures. Using Kerr microscopy to observe skyrmions for a narrow temperature and field range. With relatively low currents, it is possible to generate and move these skyrmions both within patterned wires and full films and we further have observations of the skyrmion Hall effect. The research is done in collaboration with S. A. Montoya, R. Tolley, J. Brock, S. Couture, J. J. Chess, J. C. T Lee, N. Kent, D. Henze, M.-Y. Im, S.D. Kevan, P. Fischer, B. J. McMorran, V. Lomakin, and S. Roy and is supported by the DOE.

11:40am **MI+2D-ThM12 Giant Magnetostriction and Low Loss in FeGa/NiFe Nanolaminates for Strain-Mediated Multiferroic Micro-Antenna Applications*, Kevin Fitzell*** [1]*, C.R. Rementer,* University of California, Los Angeles*; N. Virushabadoss,* University of Texas at Dallas*; M.E. Jamer,* National Institute of Standards and Technology (NIST)*; A. Barra,* University of California, Los Angeles*; J.A. Borchers, B.J. Kirby,* National Institute of Standards and Technology (NIST)*; G.P. Carman,* University of California, Los Angeles*; R.M. Henderson,* University of Texas at Dallas*; J.P. Chang,* University of California, Los Angeles

The ability to reduce the size of antennae would enable a revolution in wearable and implantable electronic devices. Multiferroic antennae, composed of individual ferromagnetic and piezoelectric phases, could reduce antenna size by up to five orders of magnitude through the efficient coupling of magnetization and electric polarization via strain. This strategy requires a low-loss magnetic material with strong magnetoelastic coupling at high frequency.

Galfenol ($Fe_{84}Ga_{16}$ or FeGa) is a promising candidate material due to its large magnetostriction (>200 ppm), large piezomagnetic coefficient (>3 ppm/Oe), and high stiffness (>50 GPa), but it is highly lossy in the GHz regime. On the other hand, Permalloy ($Ni_{81}Fe_{19}$ or NiFe) is a soft magnetic material that has very low loss in the GHz regime (ferromagnetic resonance linewidth <20 Oe) but almost no magnetostriction. In this work, nanoscale laminates containing alternating layers of FeGa and NiFe were fabricated via DC magnetron sputtering to combine the complementary properties of the two magnetic phases. Optimized magnetic laminates were shown to exhibit a small coercive field (<20 Oe), narrow ferromagnetic resonance linewidth (<40 Oe), and high relative permeability (>400) (Rementer et al., 2017). In addition, optical magnetoelastic measurements of these laminates confirmed the presence of strong magnetostriction; relative to single-phase FeGa, these laminates represent a threefold enhancement in magnetostriction at saturation and up to a tenfold enhancement at low magnetic fields.

Multiferroic composites incorporating these magnetic laminates were then studied via polarized neutron reflectometry, demonstrating coherent rotation of the individual layers' magnetization with an applied electric field across distances much larger than the exchange length of either material. Micromagnetic and finite element simulations support the experimental results, showing coherent rotation of the magnetization with only small deviations with thicker NiFe layers. Subsequent integration of these laminates into strain-mediated multiferroic antennae confirmed the absorption of electromagnetic and acoustic waves, showing great promise for the use of FeGa/NiFe laminates in micro-scale communications systems.

12:00pm **MI+2D-ThM13 Structural and Electronic Origin of Stable Perpendicular Magnetic Anisotropy in Pt/Co/Pt magnetic ultra-thin film with Ti Buffer Layer*, Baha Sakar,*** Gebze Technical University, Turkey*; Z. Balogh-Michels, A. Neels,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; O. Öztürk,* Gebze Technical University, Turkey

In this work, Pt and Co based multilayer samples with perpendicular magnetic anisotropy (PMA) are prepared. The aim of the work is the

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[1] **Falicov Student Award Finalist**

optimization and stabilization of the magnetic properties. Highly stable and repeatable PMA samples are demanded for standardization and calibration of magnetic measurements. For this purpose, Pt/Co/Pt (pcp) and Ti/Pt/Co/Pt (tpcp) samples are prepared on naturally oxidized Si(111) substrates by using magnetron sputtering. Electronic structures and elemental composition of the sample surfaces are investigated by X-Ray Photoelectron Spectroscopy. The same technique is also used for thickness calibrations of depositions. Magnetic properties of the samples are investigated by using Magneto-Optical Kerr Effect method. Orientations of the grains are important for defining the magnetic easy axis of a magnetic material. Typical symmetric XRD scans are not suitable for very thin films (<10 nm) since the signal to background ratio is low. For this reason, structural properties of the films are analyzed by using grazing angle XRD and in-plane XRD reciprocal space mapping.

Samples with the titanium buffer layer (tpcp) have perpendicular magnetic anisotropy where the pcp samples have in-plane magnetization. Structural differences in the presence of Ti layer are the strong preferred orientation for Pt, while the pcp film is random oriented. Multiple Co reflections are also visible for the pcp film. These confirmed a 111 fiber texture for the Pt in case of the tpcp sample. Contrary to that multiple Pt rings are observed for the pcp sample, which agrees with a random oriented nanocrystalline film. The lack of a texture explains the magnetic behavior.

Samples prepared in this work are used/using and studied within a joint research project, EMPIR SIB05 NanoMag funded by EURAMET.

MEMS and NEMS Group
Room 202B - Session MN+2D+AN+MP+NS-ThM

Optomechanics and 2D NEMS

Moderator: Max Zenghui Wang, University of Electronic Science and Technology of China

8:00am **MN+2D+AN+MP+NS-ThM1 Towards Microwave to Telecom Wavelength Quantum Information Transfer using Cavity Optomechanics*, John Davis,*** University of Alberta, Canada **INVITED**

The past few years have seen the rapid maturation of quantum information processors, particularly in the category of superconducting microwave circuits. With claims from leading companies that they will commercialize quantum processors in the next five years, we must wonder what quantum technologies should be developed in tandem to fully utilize these processors. For example, we are all acutely aware that while our personal computers are powerful, they are considerably more useful and interesting when networked together. So how can we likewise network quantum processors? Especially since the microwave signals of superconducting processors cannot be transmitted at room temperature without thermal decoherence. What if instead, one could link superconducting processors together through existing fiber-optic networks, which are already capable of long distance quantum information transfer? Hence the development of a transducer of quantum information from the microwave to telecom domain has become highly desirable. I will describe the current state of microwave to optical transducers, and how our lab is working towards this goal. Specifically, I will discuss the progress and challenges associated with the development of fiber-coupled telecom-wavelength cavity optomechanical resonators, and 3D superconducting microwave cavities, operating at millikelvin temperatures. I will also discuss ongoing collaborations that could enable implementation of quantum information transducers in a large-scale fiber network in Alberta.

11:20am **MN+2D+AN+MP+NS-ThM11 Reconfigurable Resonant Responses in Atomic Layer 2D Nanoelectromechanical Systems (NEMS)*, Zenghui Wang,*** University of Electronic Science and Technology of China*; R. Yang, P.X.-L. Feng,* Case Western Reserve University

Atomic layer semiconducting crystals have emerged as a new class of two-dimensional (2D) materials, exhibiting great promises for both fundamental research and technological applications. Their outstanding electromechanical properties make these materials ideal for constructing novel 2D NEMS, providing opportunities for leveraging their unique device properties across multiple information-transduction domains, at scales down to individual atomic layers. One particularly interesting category of 2D NEMS is 2D nanoelectromechanical resonators, which hold potentials for making the next generation RF signal transduction and processing components, with miniaturized size, ultra-low power consumption, and compatibility with transparent and flexible circuits. Towards future applications in the 5G era, multi-band RF signal handling capability is desired, as the number of bands each mobile device need to have access to significantly increases, and it would be impractical to simply increase the number of RF components that can only function under one RF frequency, as the space required for mounting such components scales with the number of bands. Therefore, ultralow-power tunable and reconfigurable RF devices that can adapt to different frequencies would be one solution to this challenge.

Here we present experimental demonstration of nanomechanical resonators based on layered MoS_2 atomic crystals that have reconfigurable resonant responses. By carefully studying the temperature-dependent frequency response in such MoS_2 resonators[1], we discover clear, repeatable hysteretic behavior as the device temperature is changed[2]. Leveraging this phenomenon, we achieve switchable resonance frequency f_{res} in such devices by using heating and cooling pulses. Specifically, for an example MoS_2 resonator, during heating pulses, the f_{res} decreases to ~20MHz. Once the device recovers to room temperature, f_{res} stabilizes at ~26MHz. During cooling pulses, f_{res} increases to ~29MHz, and upon reverting to room temperature f_{res} stays at ~24.5MHz, which is clearly different than the other room temperature state. Our findings suggest that such atomic-layer MoS_2 NEMS resonators could be used towards developing reconfigurable RF components whose frequency response can be switched between different states.

[1] R. Yang, et al., *IEEE UFFC, pp 198-201,* 2015. [2] Z. Wang, et al., *IEEE UFFC*, *pp* 783-786, 2015.

11:40am **MN+2D+AN+MP+NS-ThM12 Cavity Optomechanics: Dynamics and Applications*, Eyal Buks,*** Israel Institute of Technology, Israel **INVITED**

The field of cavity optomechanics deals with a family of systems, each composed of two coupled elements. The first one is a mechanical resonator, commonly having a low damping rate, and the second one is an electromagnetic cavity, which typically is externally driven. Both radiation pressure and bolometric force can give rise to the coupling between the mechanical resonator and the cavity. In recent years a variety of cavity optomechanical systems have been constructed and studied, and phenomena such as mode cooling, self-excited oscillation, and optically induced transparency have been investigated. The first part of the talk will be devoted to some dynamical effects including synchronization and intermittency. In the second part some applications of optomechanical cavities for sensitive sensing will be discussed.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+AN+EM+MI+MN+MP+PS+RM-ThM

Nanopatterning and Nanofabrication

Moderators: Brian Hoskins, National Institute of Standards and Technology (NIST), Meredith Metzler, University of Pennsylvania, Leonidas Ocola, IBM Research Division, T.J. Watson Research Center

8:00am **NS+AN+EM+MI+MN+MP+PS+RM-ThM1 Femtosecond Laser Processing of Ceria-Based Micro Actuators***, J. Shklovsky,* Tel Aviv University, Israel*; E. Mishuk,* Weizmann Institute of Science, Israel*; Y. Berg,* Orbotech Ltd, Israel*; N. Vengerovsky, Y. Sverdlov,* Tel Aviv University, Israel*; I. Lubomirsky,* Weizmann Institute of Science, Israel*; Z. Kotler,* Orbotech Ltd*; S. Krylov, Y. Shacham-Diamand,* ***Erez Benjamin,*** Tel Aviv University, Israel

The integration of piezoelectric and electrostrictive materials into micromachined Si devices is viewed as an important technological milestone for further development of Microelectromechanical Systems (MEMS). Recently, it was demonstrated that gadolinium-doped ceria (CGO) exhibits very large electrostriction effect, which results in large electrostrictive strains and high energy densities under very low frequencies (0.01 – 1 Hz). Lead-free CGO is chemically inert with respect to Si, making it an attractive candidate for implementation in MEMS actuators. However, the integration of CGO into MEMS devices is challenging due problems associated with using conventional patterning techniques involving lithography and etching.

In this work, we have successfully created functional double-clamped beam micro-actuators made of CGO films confined between the top and bottom Al/Ti electrodes. The stack containing the electrodes and the ≈ 2 µm-thick CGO film was first blanket-deposited on top of the Si wafer. Cavities were then deep reactive ion etched (DRIE) in the wafer leading to forming of the free-standing rectangular membranes, 1.5 mm × 0.5 mm in size. Finally, ≈

1.2 mm long and ≈ 100 µm wide the double-clamped beams were cut from the membranes using a femtosecond (fs) laser, demonstrating an unharmful technique for CGO patterning. Laser pulse energies, overlaps and number of line passes were varied during the experiments, to achieve successful cuts through the suspended layer by a clean ablation process. The optimized process conditions were found at a fluence of ~0.3 J/cm^2 for a pulse width of 270 fs, where minimal damage and accurate processing was achieved with minimized heat-affected zones.

Resistivity measurements between the top and the bottom electrodes before and after fs laser cutting revealed that the cutting has no influence on the electric parameters of the device and no electrical shorts are introduced by the laser processing. Vertical displacement measurements under bipolar AC voltage (up to 10 V), at the frequency range of 0.03 – 2 Hz, demonstrated the functionality of the micro-actuator. A displacement of ≈ 45 nm at the voltage of 10 V at 50 mHz was achieved. The actuator didn't show any mechanical or electrical degradation after continuous operation. Our data confirm that fs laser cutting is a useful technique for processing CGO films. The developed techniques may be expanded to other materials used for fabrication of MEMS devices, enabling fast, high yield and high-quality patterning of materials that are challenging to pattern using conventional etching-based methods.

*Three first authors contributed equally to this abstract.

8:20am **NS+AN+EM+MI+MN+MP+PS+RM-ThM2 Synthesis of Functional Particles by Condensation and Polymerization of Monomer Droplets in Silicone Oils***, **Prathamesh Karandikar**, M. Gupta,* University of Southern California

The initiated chemical vapor deposition (iCVD) process is an all-dry, vacuum process used to deposit a wide variety of functional polymers. Typically, the monomer and initiator radicals are introduced simultaneously at process conditions leading to undersaturation of monomer vapors. In this work we report a sequential vapor phase polymerization method in which monomer droplets were first condensed onto a layer of silicone oil and subsequently polymerized via a free radical mechanism to fabricate polymer particles. The viscosity of the silicone oil was systematically varied from 100 cSt through 100,000 cSt. A heterogeneous particle size distribution was produced at low viscosities of silicone oil where the smaller particles were formed by the cloaking and engulfment of monomer droplets nucleated at the vapor-liquid interface and the larger particles were formed by coalescence inside the liquid. Coalescence could be inhibited by increasing the viscosity of the silicone oil leading to a decreased average radius and a narrower size distribution of the polymer particles. A transition to polymer film formation was observed for the 100,000 cSt silicone oil substrates. We studied the polymerization of two different monomers, 4-vinyl pyridine and 2-hydroxyethyl methacrylate, since these polymers have a variety of useful properties such as pH-responsiveness and biocompatibility. Our process enables fabrication of functional particles with average diameters ranging from 100 nm – 500 nm with fast reaction times (≈ 15 min). The advantages of our method for the fabrication of polymer particles are that it does not require surfactants or organic solvents and features short reaction times compared to conventional polymer particle synthesis methods such as emulsion polymerization.

8:40am **NS+AN+EM+MI+MN+MP+PS+RM-ThM3 Competition Between Scale and Perfection in Self-assembling Structures***, **James Liddle**,* NIST Center for Nanoscale Science and Technology **INVITED**

Biology relies on self-assembly to form complex, highly-functional structures, inspiring the search for synthetic systems capable of forming similarly complex structures. Such systems typically operate under diffusion-limited, near-equilibrium conditions, making the problem even more challenging. Multi-functional, molecularly-addressable nanostructures of arbitrary shape can be built using DNA-mediated self-assembly. While this is a powerful method, and recent developments in DNA nanostructure fabrication have expanded the available design space, fabrication based on DNA alone can suffer from low yields and is hampered by the need to trade off size and mechanical rigidity.[1,2]

We have been working to both understand the factors that limit the yield of self-assembled structures, and to devise approaches to overcome them. As the number of discrete components used to assemble a structure increases, yield decreases exponentially. We circumvent this limit, by using a two-stage, hierarchical self-assembly process, which allows us to create large structures with high yield.[3] Our process employs a small number of discrete, sequence-specific elements to shape the structure at the nanoscale and define the large-scale geometry. A generic building block – a DNA binding protein, *RecA* – rigidifies the structure without requiring any unnecessary information to be added to the system.

Blending sequence-specific and structure-specific elements enables us to expand the self-assembly toolbox and make micrometer-scale, rigid, molecularly-addressable structures. More generally, our results indicate that the scale of finite-size self-assembling systems can be increased by minimizing the number of unique components and instead relying on generic components to construct a framework that supports the functional units.

[1] Murugan, A., Zou, J. & Brenner, M. P. Undesired usage and the robust self-assembly of heterogeneous structures. *Nat. Commun.* **6**, 6203, doi:10.1038/ncomms7203 (2015).

[2] Schiffels, D., Liedl, T. & Fygenson, D. K. Nanoscale structure and microscale stiffness of DNA nanotubes. *ACS Nano* **7**, 6700-6710, doi:10.1021/nn401362p (2013).

[3] Schiffels, D, Szalai, V. A., Liddle, J. A., Molecular Precision at Micrometer Length Scales: Hierarchical Assembly of DNA–Protein Nanostructures, *ACS Nano*, **11**, 6623, (2017)

9:20am **NS+AN+EM+MI+MN+MP+PS+RM-ThM5 Polymer Templated Annealing of DNA Patterned Gold Nanowires***, **Tyler Westover**, B. Aryal, R.C. Davis, A. Woolley, J. Harb,* Brigham Young University

Using DNA origami as a bottom up nanofabrication technique, gold nanowires are formed via directed assembly of gold nanorod seeds and connected by electroless plating. This metal deposition process results in wires with low conductivities compared to bulk gold. Junctions between plated seeds are likely the cause of this low conductivity. Annealing of the nanowires could potentially improve the conductance, however, nanowire annealing at low temperatures (200° C) results in wires coalescing into beads. A polymer encapsulation layer was deposited to maintain overall nanowire shape during annealing. The polymer templated anneal resulted in a resistance reduction, in some cases, to below 1000 ohms. Resistance measurements were performed using a four point resistance configuration. Electrical contacts to the randomly oriented 400 nm long wires were made by electron beam induced deposition. Nanowire morphology was measured before and after annealing by scanning electron and high resolution transmission electron microscopy.

11:00am **NS+AN+EM+MI+MN+MP+PS+RM-ThM10 Directed Self-assembly of Block Copolymers for Applications in Nanolithography***, **Paul Nealey**,* University of Chicago **INVITED**

DSA of block copolymer films on chemically nanopatterned surfaces is an emerging technology that is well-positioned for commercialization in nanolithography and nanomanufacturing. DSA of (PS-b-PMMA) films on lithographically defined chemically nanopatterned surfaces is one focus of our activities in which the main research objectives revolve around understanding the fundamental thermodynamics and kinetics that governs assembly, and therefore patterning properties such as 3D structure, perfection, and processing latitude. A second focus is to use the physical and chemical principles that we have elucidated for DSA of PS-b-PMMA towards the development of block copolymer systems capable of self-assembling into the sub 10 nm regime and continuing to meet the stringent constraints of manufacturing. The research is enabled by the recent development of techniques to combine metrology tools (TEM tomography, GISAXS, RSoXS, high-speed APF), theoretically informed course grained models, and evolutionary algorithms to quantitatively determine and predict the independent process and material parameters that result in different 3D structures of assembled domains.

11:40am **NS+AN+EM+MI+MN+MP+PS+RM-ThM12 Three Dimensional Mesoporous Silicon Nanowire Network Fabricated by Metal-Assisted Chemical Etching***, **Deepak Ganta**, C. Guzman, R. Villanueva,* TAMIU

Mesoporous nanowires have gained huge attention due to their applications in energy and sensing. The high surface area along with the quantum confinement effect lead to improved performance of the electrochemical devices during energy conversion and storage. 3D structure or nanowire network improves the reaction site surface area even further along all the three dimensions, enhancing both light and heat absorption. There is also a huge demand for inexpensive, non-lithographic methods to fabricate 3D network of nanowires, which are also mesoporous, with better control of both dimensions and porosity, over a large surface area. They can be very useful in some broad range applications such as solar energy conversion, energy storage, water harvesting, environmental control, bio-sensing, and thermoelectrics.

To address the problem, we report a simple and inexpensive method of fabricating 3D mesoporous Si nanowire network by metal-assisted chemical etching (MacEtch). Degenerately doped p-type silicon or p+ silicon wafer (0.001 ~0.005 Ω·cm) was coated with about 22 nm silver film at 350 °C for 5~6 hours in a vacuum furnace (pressure < 3×10 $^{-}$7 Torr). Scattered silver particles with different sizes were formed as a result of the dewetting process. Then we deposited 10~11 nm of noble metal (Au) at 0.5 Å/s rate, followed by silver lift-off to obtain an Au mesh as an etching mask. The mixture of a chemical solution of HF: H_2O_2: Ethanol = 30:1:1 is used as a chemical etchant under room temperature. The time of immersion of the silicon wafer in the etchant effects the aspect ratio of the silicon nanowire array. After MachEtch, the Au is removed by immersing the sample in the aqua regia solution. The ratio of the chemicals in the etchant will affect the pore size. The aspect ratio of the silicon nanowire network can be controlled by the etching rate. The etching rate was roughly one µm/min. The 3D network is formed as the length of the 1D silicon nanowires (50 nm -100 nm) was varied, followed by critical point drying to carefully control the uniformity of 3D silicon nanowire network on the entire surface area of the 6-inch silicon wafer.

Analysis of the 3D mesoporous silicon nanowire network was conducted using Scanning Electron microscopy (SEM), and the top view image confirmed the 3D network of silicon nanowires. The pore sizing (2-50 nm) along with the crystallinity confirmed from the high-resolution transmission electron microscopy (TEM) images with the diffraction patterns.

12:00pm **NS+AN+EM+MI+MN+MP+PS+RM-ThM13 Enhancing Light Extraction from Free-standing InGaN/GaN light Emitters Using Bio-inspired Backside Surface Structuring***, L. Chan, C.D. Pynn, S.P. DenBaars,* ***Michael Gordon,*** University of California at Santa Barbara

A simple, scalable, and reproducible nanopatterning method to create close-packed (moth-eye like) patterns of conical nano- and microscale features on InGaN/GaN LED surfaces, and on the backside outcoupling surface of LED devices, is presented. Colloidal lithography via Langmuir-Blodgett dip-coating using silica masks (d = 170–2530 nm) and Cl_2/N_2-based plasma etching produced features with aspect ratios of 3:1 on devices grown on semipolar (20-21) GaN substrates. The resulting InGaN/GaN multi-quantum well (MQW) structures were optically pumped at 266/405 nm, and light extraction enhancement was quantified using angle-resolved photoluminescence (PL). A 4.8-fold overall enhancement in light extraction (9-fold at normal incidence) relative to a flat outcoupling surface was achieved using a feature pitch of 2530 nm. Extraction enhancement occurs due to the graded-index (GRIN) effect and breaking of the TIR condition via increased diffuse scattering and diffractive effects, the importance of which evolves with moth-eye feature size. PL results also demonstrate that colloidal roughening, which has greater geometric tunability and works on any GaN orientation, is equivalent to current, c-plane only photoelectrochemical (PEC) roughening methods. Patterning the outcoupling backside of a semipolar device, rather than the topside, is also a technologically feasible approach to fabricate electrically pumped devices because it avoids issues associated with making large area (topside) p-contacts, etching close to or into the active emitter region (destroying the MQWs), or disrupting guided modes in thin-film LEDs layers on sapphire. Because of its simplicity, range of optical control, and wide substrate compatibility, the colloidal lithography technique is a promising alternative to existing commercial processes and a future pathway for enhanced extraction engineering in free-standing polar, nonpolar, and semipolar III-nitride LEDs.

Plasma Science and Technology Division
Room 104C - Session PS+EM+TF-ThM

Atomic Layer Processing: Atomic Layer Etching

Moderators: Erwin Kessels, Eindhoven University of Technology, The Netherlands, Mingmei Wang, TEL Technology Center, America, LLC

8:00am **PS+EM+TF-ThM1 Precise Flux Control of Ions and Radicals using Electron Beam Generated Plasmas***,* ***David Boris,*** U.S. Naval Research Laboratory **INVITED**

Processing with atomic layer precision requires the ability to not only add, remove or modify one monolayer of material but to also leave adjacent layers unchanged. This requires fine control over the flux of species and energy deposition at the surface. In addition to the need for low damage, the complex device structures proposed for next generation nano-electronics will require control over radical to ion ratio as well. Electron beam-generated plasmas are generally characterized by high charged particle densities (10^{10}- 10^{12} cm^{-3}), low electron temperatures (0.3 - 1.0 eV), and in reactive gas backgrounds, a relatively low radical production rate compared to discharges. These characteristics provide the ability to precisely control the ion energy at adjacent surfaces and importantly, also the ability to control the ratio of ion to radical fluxes. In this work, we demonstrate this precise level of control using a variety of plasma characterization techniques and demonstrate how the applicability of these features to the processing of select materials systems. Specifically, we will discuss the processing of monolayer material systems such as graphene and MoS_2, where the material properties can be tuned without unwanted erosion or damage. Also SiN etching using pulsed, electron beam generated plasmas produced in SF_6 backgrounds is examined with particular attention paid to the etch rates, selectivity (vs. carbon films, Si and SiO_2), and patterning as function of operating parameters such as relative gas concentration, operating pressure, and substrate bias. Lastly, we address the use of electron beam generated plasmas for native oxide removal and subsequent passivation of surfaces. The processing results are compared with plasma diagnostics to gain a better understanding of the process requirements. This work is partially supported by the Naval Research Laboratory base program.

8:40am **PS+EM+TF-ThM3 Demonstration of Self-limiting Nature and Selectivity Control in Annealing Procedures for Rapid Thermal-Cyclic ALE of W, TiN, and SiN***,* ***Kazunori Shinoda****, H. Kobayashi,* Hitachi, Japan*; N. Miyoshi, K. Kawamura, M. Izawa,* Hitachi High-Technologies, Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Isotropic atomic layer etching (ALE) is expected to play an important role in semiconductor manufacturing because the next-generation devices will have miniaturized three-dimensional structures. The authors have developed isotropic ALE for SiN, TiN, and W using rapid thermal-cyclic processes, which are cyclic repetitions of plasma exposure and infrared annealing [1, 2]. Isotropic ALE ideally consists of cyclic repetitions of self-limiting formation and self-limiting desorption of the surface-modified layers. In the previous publications, the authors demonstrated self-limiting nature of the plasma exposure steps. In this paper, self-limiting nature of the infrared annealing steps are demonstrated. It is also demonstrated that etching selectivity between different materials can be controlled to be from infinitely selective to nonselective by adjusting the infrared annealing time.

The experimental apparatus used in this study is an ALE tool for 300-mm wafers. This tool is composed of a processing chamber, an inductively-coupled plasma source, infrared lamps, and in-situ ellipsometer. Films of W, TiN, and SiN deposited on Si substrates were used as sample materials. The wafers were first exposed to hydrofluorocarbon-based plasma to produce surface-modified layers on the surfaces of the materials to be etched. The wafers were then annealed by infrared irradiation to remove the surface-modified layers. The cycle of plasma exposure and infrared annealing was repeated ten times.

Firstly, infrared annealing time dependence of wafer temperature was examined. It was found that wafer temperature increased with increasing irradiation time at around 7°C /sec. Next, we examined how the annealing time affected the etched amount per cycle for W, TiN, and SiN. In the experiment, ten-cycle etching was repeated changing the annealing time in the range from 0 to 24 sec. The etched amount per cycle for W increased with the annealing time and saturated when the annealing time exceeded 10 sec. The etched amount per cycle for TiN increased when the annealing time exceeded 10 sec and saturated when the annealing time exceeded 20 sec. The etched amount per cycle for SiN saturated when the annealing time exceeded 15 sec. These results imply that the ALE process for W, TiN, and SiN are self-limiting in nature. Moreover, by choosing an optimal infrared annealing time, both highly selective and nonselective ALE for different materials was obtained. For instance, infinitely selective ALE of W over TiN was achieved when infrared annealing time was 8 sec.

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

[2] K. Shinoda et al., SPIE Advanced Lithography 10589-17 (2018).

9:00am **PS+EM+TF-ThM4 Mechanisms for Atomic Layer Etching of Metal Films by the Formation of Beta-diketonate Metal Complexes*, Tomoko Ito,*** *K. Karahashi, S. Hamaguchi,* Osaka University, Japan

Ar$^+$ ion milling processes have been widely used for the fabrication of magnetic tunnel junctions (MTJ) of magnetoresistive random access memory (MRAM) devices. However, Ar$^+$ ion milling has a problem of surface damage caused by high energy ion bombardment, so the development oflow-energy reactive ion etching (RIE) processes is imperative for further miniaturization of MTJ cells. In recent years, beta-diketones such as acetylacetone (acac) andhexafluoroacetylacetone (hfac) have been considered as efficient etchants for thermal atomic layer etching (ALE) of metal films by the formation of volatile beta-diketonate metal complexes. Moreover, if low-energy ion incidence, rather than heating of the substrate, enhances the formation of organic metal complexes and their desorption from the metal surface, anisotropic ALE of metal films may be achieved. In this study, we explore the possibility of the development of such ion-enhanced metal surface etching using surface reactions of beta-diketones. The objectives of our research are, therefore, to understand surface reactions between gas-phase beta-diketones and metal surfaces and to clarify the beam-surface interaction between low-energy Ar$^+$ ions and beta-diketone adsorbed metal surfaces. To achieve these objectives, we have developed an atomic layer process (ALP) surface analysis system, which consists of a high-resolution X-ray photoelectron spectroscopy (XPS) analysis chamber and an ALP reaction chamber. The system allows *in-situ* analyses of, e.g., acac orhfac adsorbed Cu, Ni and Co surfaces and those after an exposure to low-energy Ar$^+$ or Xe$^+$ ion fluxes. The typical reactive gas exposure was in the range of 100 -10000 L (in units of L: Langmuir: 10^{-6} Torr・s) and the ion energy was in the range of 10- 50 eV. It is found that, for pre-oxidized Ni and Cu surfaces, hfac molecules adsorbed without C-O and C-F bond braking. It is also found that low-energy Ar$^+$ ion injection breaks down adsorbed hfac molecules even on a pre-oxidized Ni surface, fluorinating the Ni surface. The results show the difficulty of using low-energy ion exposure to enhance the formation of volatile metal complexes but also suggests a possibility of atomic-level surface modification of metal films using organic molecules, which may be used for highly controlled etching processes.

9:20am **PS+EM+TF-ThM5 Thermal Atomic Layer Etching of Transition Metal Films*, Charles Winter,*** Wayne State University **INVITED**

Atomic layer deposition (ALD) features self-limited growth, which affords inherently conformal coatings on shaped substrates and Ångstrom-level thickness control.[1] Atomic layer etching (ALE) is a related technique, where layers in a film are removed one layer at a time and involve a self-limited mechanism.[2] Until recently, almost all ALE processes entailed either plasmas or ion beams.[2] Plasmas and ion beams require expensive equipment and the energetic species may damage sensitive layers in films. As a result, there is considerable interest in the development of purely thermal ALD processes that use chemical reactions to achieve thickness reductions. The first thermal ALE processes were only reported in 2015 for metal oxides and fluorides,[3-5] and many materials can now be etched thermally. Cobalt, copper and other first row transition metal films have wide applications in microelectronics devices.[6] The ability to carry out ALE on these metals would be very valuable. However, there has been little progress reported to date in the thermal ALD of first row transition metal films. We recently reported the ALD growth of cobalt[7] metal films and have explored these films as starting substrates in thermal ALE. In this talk, we will give an overview of the thermal ALE of cobalt metal films. These processes entail treatment of the cobalt metal films with formic acid in a first step, presumably to afford surface layers of cobalt(II) formate. These oxidized surfaces are then treated with various ligands in a second step to afford volatile cobalt(II) complexes, resulting in etching. Ligands that can be used to promote etching will be overviewed. Thermal ALE of copper and other metal films will also be presented.

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11:00am **PS+EM+TF-ThM10 Gas Cluster Ion Beam Etching under Organic Vapor for Atomic Layer Etching*, Noriaki Toyoda,*** University of Hyogo, Japan **INVITED**

In our presentation, we will present our investigation of the usage of a gas cluster ion beam (GCIB) under organic vapor to irradiate a surface to produce atomic layer etchings (ALE). Gas cluster ions are aggregates of thousands of atoms or molecules that are collectively ionized and can be focused into a GCIB. The kinetic energy of a gas cluster ion is shared between the thousands of gas atoms or molecules; hence, the energy per particle in the cluster can be easily reduced to several eV. Furthermore, gas cluster ions can transfer a relatively large amount of energy to a concentrated area of the target surface; thus, a large number of target atoms can be sputtered by one gas cluster ion. As a result of the high-energy impact of gas cluster ions, low-damage surface modification takes place. Because of the features outlined above, GCIB guns are also widely used in conjunction with surface analysis techniques such as secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS).

Because gas cluster ions deposit energy in a condensed manner without severe damage, surface reactions are enhanced even at room temperature, which is beneficial for ALE. In our study, we performed halogen-free ALE of Cu using oxygen-GCIB irradiation under acetic acid vapor [1]. We performed the etching process in the following steps: (1) adsorption of acetic acid on Cu, (2) evacuation of residual acetic acid vapor, and (3) reaction between acetic acid and Cu with the subsequent removal of the surface Cu layer via oxygen-GCIB irradiation. During one cycle of ALE, a very thin layer of acetic acid was adsorbed onto the Cu. Subsequently, the chemically altered Cu on the surface layer was removed with oxygen GCIB irradiation. When the Cu surface was irradiated with a 20 kV oxygen GCIB, Cu atoms beneath the surface layer were also sputtered after the removal of the chemically modified layer and as a result, this etching process was not self-limiting. On the contrary, when the surface was irradiated with a 5 kV oxygen GCIB, Cu atoms beneath the surface layer were not sputtered after the removal of the chemically modified layer. Thus, it could be concluded that halogen-free ALE could only be achieved at a lower oxygen GCIB voltage, namely 5kV. In the presentation, we will report the preliminary results of the various metal etching experiments we conducted with a GCIB under organic vapors and report their applications for ALE.

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11:40am **PS+EM+TF-ThM12 Utilizing Chemical Structure of Hydrofluorocarbon Precursors to Achieve Ultra-High Selective Material Removal in Atomic Layer Etching*, Kang-Yi Lin,*** *C. Li,* University of Maryland, College Park*; S.U. Engelmann, R.L. Bruce, E.A. Joseph,* IBM Research Division, T.J. Watson Research Center*; D. Metzler,* IBM Research Division, Albany, NY*; G.S. Oehrlein,* University of Maryland, College Park

Atomic layer etching (ALE) applies sequential deposition and etching steps with short processing step length to establish selective material removal and atomic scale precision. The reactant pulsed in the ALE sequential reaction steps may behave differently from its use in continuous plasma etching, since for ALE the reactant is injected only during the deposition step and the deposited film undergoes non-steady-state surface desorption reaction during the etching step. In this work we will compare a mixture of a fluorocarbon (FC) precursor and H_2 with a hydrofluorocarbon (HFC) precursor, i.e. mixtures of octafluorocyclobutane (C_4F_8) with H_2 and 3,3,3-trifluoropropene ($C_3H_3F_3$), for SiO_2 ALE and etching of SiO_2 selective to Si_3N_4, Si and SiGe. For continuous plasma etching, process gas mixtures, e.g. C_4F_8/H_2, have been employed and enable highly selective material removal based on reduction of the fluorine content of deposited steady-state HFC films. This approach, however, is not successful for ALE since the residual hydrogen during reaction steps will induce etching and reduce the remaining thickness of the deposited HFC film. This HFC film on the surface is required for both etching of SiO_2 and passivation of the Si_3N_4, Si and SiGe, and a reduction in film thickness leads to lower material etching selectivity. $C_3H_3F_3$ with hydrogen reduces fluorine content in the precursor structure and allows deposition of fluorine-deficient HFC films without suppressing the formation of the passivation layer on the surface. Our results support that gas pulsing of complex HFC precursors in ALE provides a novel opportunity of utilizing the precursor chemical structure for achieving near-atomically abrupt selective ALE processes for SiO_2 over Si_3N_4, Si, SiGe and potentially for other materials. The authors gratefully acknowledge financial support of this work by the Semiconductor Research Corporation (2017-NM-2726).

12:00pm **PS+EM+TF-ThM13 Etch Selectivity Mechanisms of Implanted Over Pristine SiN Materials in NH_3/NF_3 Remote Plasma for Quasi Atomic Layer Etching with the Smart Etch Concept***, Vincent Renaud, E. Pargon, C. Petit-Etienne,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; J.-P. Barnes, N. Rochat,* Cea, Leti, Minatec, France*; L. Vallier, G. Cunge, O. Joubert,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

The complexification of 3D architectures of advanced CMOS devices require to etch materials with a sub-nanometer accuracy without introducing damage to the surface and with infinite selectivity between the materials in presence. The Smart etch concept is a n original etching approach which has successfully been proposed to etch silicon nitride spacer with less than 1nm of spacer dimension loss and SiGe recess. This technic relies on a surface modification by H or He ion implantation performed in capacitive coupled plasma (CCP) reactor, followed by a selective removal of the modified layer over the pristine material. The selective removal can be achieved either by wet or remote plasma source etching. Today, the mechanisms driven the etch selectivity between the pristine and modified SiN layers in remote plasma are still misunderstood

In this paper, we propose to investigate the etching mechanisms of pristine and implanted silicon nitride layers in NH_3 /NF_3 remote plasma. The etching experiments are performed in 300mm industrial prototype of reactor, equipped with both a CCP and a remote plasma source allowing to achieve the implantation and the removal steps in the same reactor chamber. The substrate temperature can be varied from 40 to 200°C during the process. The etching kinetics are followed in real time thanks to in situ kinetic ellipsometry. The SiN layers are characterized by XPS, XRR and Tof-SIMS.

The real time monitoring of the etching reveals that there is a delay before the SiN layers are etched for any plasma conditions and wafer temperature. The incubation time increases with substrate temperature and depends on the surface state. For instance, our results show that a deoxidized SiN surface using HF wet is not etched in NH_3/NF_3 remote plasma, proving that the oxygen acts as a catalysis of the reaction, and subsequent material etching. Moreover, it is shown that the main impact of the He or H_2 implantation step is to functionalize the SiN surface by implanting residual oxygen present in the chamber and generating dangling bond. Thus, the incubation time when etching implanted SiN layers in NH_3/NF_3 plasma at 100°C is only of 30s compared to 84s for pristine SiN. This means that short duration of remote plasma is the key parameter to achieve, infinite selectivity between implanted and pristine SiN surface.

Plasma Science and Technology Division
Room 104A - Session PS-ThM

Plasma Sources

Moderators: TaeSeung Cho, Applied Materials, GeunYoung Yeom, Sungkyunkwan University, Republic of Korea

8:00am **PS-ThM1 Model of a Radio-Frequency Low Electron Temperature Plasma Source***, **Shahid Rauf**, L. Dorf, K.S. Collins,* Applied Materials

The time-averaged plasma potential in a partially ionized plasma is directly linked to the electron temperature (T_e). Plasmas with low T_e or plasma potential are attractive for applications that require low ion energy at surfaces. One of the most promising such applications is atomic layer etching. Reactive ion etching relies on reaction of energetic ions and chemically reactive radicals on surfaces for material removal. Ion energy in radio-frequency (RF) plasmas is typically 10s of eV or higher. Since such energetic ions can damage and modify the near-surface material, film etching with atomic precision becomes impractical using low pressure RF plasmas. On the other hand, if the plasma potential is low and capability exists to control the ion energy at the substrate using RF or DC biasing, one can etch material with Å-scale fidelity [1]. Even conventional plasma processes can benefit from low T_e as plasma potential determines the energy of ions bombarding the chamber surfaces.

This paper describes a radio frequency (RF) driven low T_e plasma source. This source utilizes two RF supplies, a higher frequency source (60 MHz) for plasma production and a lower frequency source (2 MHz) for controlling the ion energy. The plasma source is divided into two regions separated by a perforated plate. A high density (> 10^{17} m^{-3}) plasma is generated in the primary region next to the RF powered electrode. The DC bias on the powered electrode is high (~ 2000 V) leading to energetic ion bombardment on it. These ions produce secondary electrons that, under the low-pressure condition under consideration, enter the plasma as a beam of energetic electrons and many of them reach the perforated plate. It is demonstrated that the slits in the perforated plate can be designed to prevent the RF primary plasma from leaking into the secondary region while still allowing the beam electrons to pass through. The plasma produced by the beam electrons has moderate density (~ 10^{16} m^{-3}) and T_e < 0.5 eV. The influence of slit dimensions on the characteristics of the plasma in the secondary discharge region is examined in the paper.

[1] L. Dorf, J. C. Wang, S. Rauf, G. A. Monroy, Y. Zhang, A. Agarwal, J. Kenney, K. Ramaswamy and K. Collins, J. Phys. D 50, 274003 (2017).

8:20am **PS-ThM2 Electron-beam Sustained Plasma with Unique Characteristic of Low Electron Temperature at Very Low Pressure***, **Zhiying Chen**,* Tokyo Electron America, Inc.*; K. Nagaseki,* Tokyo Electron Miyagi, Ltd., Japan*; J. Blakeney, M. Doppel, P.L.G. Ventzek,* Tokyo Electron America, Inc.*; A. Ranjan,* TEL Technology Center, America, LLC.

Low electron temperature plasmas have recent interest because of their potential applications in atomic layer etching, etch of non-volatile materials and polymer processing. Electron-beam sustained plasmas (ESP) are primarily sustained by an electron beam. In this presentation we describe one kind of ESP system consisting of two plasmas separated by a dielectric injector. The electron-source plasma is generated by an inductively coupled source (ICP), on the boundary walls of which a negative DC voltage is applied. The main plasma is the ESP itself, which is generated by the electron beam extracted from ICP through a dielectric injector by an accelerator located inside the ICP. The electron temperature and electron energy distribution functions (EED*f*) are measured by Langmuir Probe. We show the ESP plasma is characterized by a low electron temperature (less than 1eV) at very low pressure (1-10mT) measured. This unique characteristic is unavailable to conventional plasmas, in which pulsing or high pressure is required to obtain low electron temperature. The plasma also illustrates the controllable EED*f* especially when superposed on an additional plasma such as a simple ICP source. The electron temperature of the ICP source can be significantly dropped with the addition of an ESP. The presentation includes a discussion regarding the uniformity and scalability of the ESP system. In particular, the generation of a sheet electron beam without the aid of a magnetic field and the impact of externally coupled capacitive power are discussed.

8:40am **PS-ThM3 Hydrid Plasma Source with Inductive and Capacitive Fields: Fundamental Understanding and Nano-applications***, **Hyo-Chang Lee**,* Korea Research Institute of Standards and Science (KRISS) **INVITED**

Hybrid plasma source with inductive and capacitive fields, which is often called RF-biased inductively coupled plasma (ICP) or reactive ion etcher, has been widely used in semiconductor, display, and solar-cell etching processes [1]. The original concept for the hybrid plasma source is an expectation that the antenna coil of the ICP controls the plasma density while the RF bias controls the ion energy independently. However, the RF bias can act as plasma source like an asymmetric capacitively coupled plasma (CCP) and directly affect plasma parameters such as electron temperature, plasma density, and electron energy distribution. In this talk, I will present effects of inductive and capacitive fields of the hybrid plasma source on the plasma parameters, electron heating, and processing result [2-9]. This invited talk will find the fundamental understanding of the hybrid plasma source and give open possibilities for applications to various applied fields to find novel control knob and optimizing processing conditions for improvement of the device quality and processing results.

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[2] Lee et al., Appl. Phys. Letts. 96, 071501 (2010).

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[5] Lee et al., Appl. Phys. Letts. 101, 244104 (2012).

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[9] Lee et al., Plasma Sources Sci. Technol. 24 0240 (2015).

9:20am **PS-ThM5 Improving RF Power Delivery for Pulsed Operation**, *J. Brandon, C. Smith, K. Ford,* North Carolina State University; *S.K. Nam,* Samsung Electronics; ***Steven Shannon,*** North Carolina State University

The increased reliance on pulsed RF power delivery for manufacturing applications has greatly expanded the process window and performance capability of state-of-the-art process equipment. Power delivery under pulsed conditions rely mainly on static impedance matching conditions, delivered power compensation, or optimization algorithms that minimize power reflection due to impedance mismatch over multiple pulse cycles. On time scales within the RF pulse, power delivery can significantly impact process performance, particularly as devices approach the sub 10nm regime, as it can impact electron temperature spikes at ignition and the formation of electric potentials in and around the plasma and substrate. Options to improve power delivery efficiency within the pulse can provide mechanisms to control or mitigate these conditions for process optimization, but have practical limitations due to the ms time scale response needed to capture electrical transients under pulsed conditions.

Using standard match topologies found in pulsed RF systems, methodologies for impedance matching optimization for plasma transient control are presented. Using a simple global plasma model with equivalent circuit module for capturing power delivery circuitry and a cylindrical ICP reactor, the interaction between power coupling (specifically impedance matching) and plasma conditions during the power-on transient of a pulsed ICP system are studied. Control of electron temperature spiking at the power onset as well as rate of rise of plasma density are demonstrated using a static p-type match topology. The impact of dissipative losses in the matching network are also explored, and suggest that the standard insertion loss, or “equivalent series resistance” characterization of impedance match power dissipation may present an incomplete picture of match performance under transient conditions and that dissipation in the shunt elements play a significant role with regard to the transient plasma conditions during the power on cycle of a pulsed RF system, and may provide a pathway for improving the efficiency of power delivery during pulsed operation. Finally, a synergistic approach where match topology, source antenna design, and plasma load are considered can provide pathways for within-pulse impedance matching and power delivery control. We will present examples where this approach may enable within-pulse active tuning of pulsed RF systems with existing technologies. This work is supported by the Samsung Mechatronics R&D Center.

9:40am **PS-ThM6 Optimizing Transients Using Low-High Pulsed Power in Inductively Coupled Plasmas**, ***Chenhui Qu,*** *S.J. Lanham,* University of Michigan; *T. Ma, T. List, P. Arora, V.M. Donnelly,* University of Houston; *M.J. Kushner,* University of Michigan

Pulsed inductively coupled plasmas (ICPs) are widely used for etching in semiconductor device fabrication. Pulse repetition frequencies (PRFs) of up to 10s kHz are commonly used for the high power density provided during the pulse-on period and the unique chemistry during the pulse-off period. The use of highly attaching halogen gases produces low electron densities during the pulse-off period, which can produce instabilities, E-H transitions and ignition delays when applying power. To mitigate these issues, a low-level power could be maintained during “pulse-off” to limit the minimum plasma density, therefore reducing ignition delays and enhancing plasma stability.

In this work, ICPs sustained by 1-5 kHz pulsed power using Ar/Cl_2 mixtures at tens of mTorr were computationally and experimentally studied. The computations were performed with the 2-D Hybrid Plasma Equipment Model. The experiments include measurements of electron density (n_e), temperature (T_e) and electron energy distributions. The power is modulated during the pulse-off period and the transient behavior of the ICP was studied.

The computed T_e reaches a quasi-steady state for both high and low power excitation. Some experimental results agree well with the predictions from the model while others show a reproducible delay in plasma ignition. The model predicts that within the skin-depth, T_e spikes to a high value during the low-to-high power modulation and a low value during a high-to-low power modulation. Due to some averaging and energy loss that occurs during transit from the skin depth, both measurements and model results show little modulation in T_e a few cm above the substrate. The influence of the power, pressure, PRF and duty cycle of the pulse profile on the bulk plasma properties will be discussed.

* Work supported by Samsung Electronics Co. Ltd., National Science Foundation and the DOE Office of Fusion Energy Sciences.

11:00am **PS-ThM10 Silicon Nitride Film Formations Using Magnetic-Mirror Confined New Plasma Source**, ***Tetsuya Goto,*** Tohoku University, Japan; *S.K. Kobayashi,* Kotec Company, Ltd., Japan; *S. Sugawa,* Tohoku University, Japan

Realization of high-quality silicon nitride film formation at low temperature was strongly required for various fields such as the Si CMOS devices, the solar cells, as well as the micro electro mechanical systems (MEMS). In this study, a magnetic-mirror confined electron cyclotron resonance plasma source for low-damage plasma processings was newly developed, and applied to the silicon nitride film formations. The mirror-confined plasma is the well known concept in a field of fusion plasmas where high-density and high-temperature plasmas are produced by confining plasmas using the magnetic field. We applied this concept to plasma enhanced chemical vapor depositions. In a magnetically confined plasma, neutral reactive species produced by the plasma can escape from the confined plasma without the restriction of motion by the magnetic field, contrary to the confined charged particles of ions and electrons. Thus, when the substrate is placed at the neighborhood of the confined plasma, a large amount of reactive species will be supplied to the substrate with low irradiation of ion flux, suggesting the realization of low-damage and high-quality processes. It was found that the magnetic mirror confinement method worked well to excite the high-density plasma larger than 10^{11} cm^{-3} with low plasma excitation power of 10 W or less. SiN films were deposited by exciting $Ar/SiH_4/N_2/H_2$ plasmas. It was found that, in the optimized condition, an impurity concentration of oxygen in the film could be suppressed less than 1%, which was even smaller than that in the controlled low-pressure chemical-vapor deposited film at 750°C, suggesting the realization of high-quality nitridation process. Next, wet etching stability was investigated by dipping the films into the 5% HF solution. For the 400°C-deposited film, the etching rate was approximately 3 nm/min which was the same level to that of 750°C-LPCVD film. Although the etching rate of the 200°C-deposited film increased to approximately 10 nm/min, this rate was much smaller than that of thermally-grown SiO_2 film (approximately 40 nm/min).

It was also confirmed that the excellent step coverage could be obtained for the 0.5 micron trench pattern.

The developed plasma source has a potential to realize high-quality film deposition processes of the plasma CVD, the plasma ALD, and the reactive sputtering.

Acknowledgement

The deposition process was carried out in Fluctuation-Free-Facility in Tohoku University.

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2. T. Goto, K. Sato, Y. Yabuta, S. Hara and S. Sugawa, Journal of the Electron Devices Society, vol. 6, (2018) 512.

11:20am **PS-ThM11 Resonant Element Microwave Plasma Source**, ***Barton Lane,*** *P.L.G. Ventzek, A. Bhakta,* Tokyo Electron, America, Inc.; *K. Nagaseki,* Tokyo Electron Miyagi, Ltd.; *A. Ranjan,* Tokyo Technology Center America

We report here the use of resonant elements for plasma generation. The resonant elements are realized as metal structures embedded in alumina using a metal printing and lamination process. The embedded structures present a flat featureless alumina face to the plasma which is optimal for reducing particle generation. The structures are chosen to be resonant in the microwave frequency range and thus have geometric sizes of approximately 10 mm, although this can be chosen for the particular application. The structures can be viewed as LC circuits which have a number of resonances in the microwave band each with a corresponding spatial electric field eigenmode. The geometry of the structures reported here positions the inductive portion near to the plasma and in one eigenmode produces inductively generated circular mirror currents in the plasma which have a spatial dimension of 10 mm. The LC structures which we report on have a quadrupole symmetry in order to minimize the coupling to surface waves which tend to propagate away from the launch structure and are difficult to control. The fields responsible for plasma generation are the near fields of the resonant structure and these die away quickly from the structure giving a localized plasma generation region. The alumina blocks in which the resonant element structures are embedded are pierced by cylindrical holes through which gas is injected into the generated plasma. For one eigenmode of this system at low pressures (~ 10 mTorr) the electric fields are such that the plasma concentrates in the supersonic gas jet and has a size of approximately 1 mm. The structures can also be used to sustain a plasma in a high pressure cavity which then serves as a source of radicals through jet outlets. In this case the cavity pressures are in the several Torr or higher range. With the addition of small permanent magnets operation in the 0.1 mTorr regime is possible by exploiting the electron cyclotron phenomenon. The resonant elements can be arranged in an array. We report on a linear array which is coupled by TEM parallel plate transmission lines embedded in the alumina. Because the presence of plasma tends to detune the structures from resonance there is a natural negative feedback which helps to balance the multiple elements producing a reasonably uniform “curtain” of plasma. The ability to extend such an array to cover the entire upper electrode of a semiconductor reactor has been noted as well as the ability to control the spatial distribution by choosing different natural resonances for different regions of the reactor.

11:40am **PS-ThM12 Microwave Plasma Enabling Efficient Power-To-X Conversion***, **Gerard van Rooij,*** DIFFER, The Netherlands **INVITED**

Sustainable energy generation by means of wind or from solar radiation through photovoltaics or concentrated solar power will continue to increase its share of the energy mix. Intermittency due to e.g. day/night cycle, regional variation in availability, and penetration of sustainable energy into sectors other than electricity such as the chemical industry necessitates means of storage, transport and energy conversion on a large scale. A promising option is the synthesis of chemicals and artificial fuels using sustainable energy. A truly circular economy requires that the raw materials are the thermodynamically most stable ones such as CO_2 and N_2. In this contribution it will be highlighted how plasma chemistry can potentially combine compatibility with e.g. intermittency and localized production to activate these molecules with maximum energy efficiency, essentially due to preferential vibrational excitation (causing inherently strong out-of-equilibrium processing conditions that achieve selectivity in the reaction processes). Examples will be discussed of research carried out at DIFFER to ultimately enable a scale up to chemical industrial applications.

A common microwave reactor approach is evaluated experimentally with laser Rayleigh and Raman scattering (to assess gas and vibrational temperatures) and Fourier transform infrared spectroscopy (yielding conversion and efficiency). For example, 50% energy efficiency was observed in pure CO_2 (forming CO and O_2) in a thermodynamic equilibrium conversion regime governed by gas temperatures of ~3500 K. These results are interpreted on basis of Boltzmann solver based plasma dynamics estimates, indicating that intrinsic electron energies are higher than what is favourable for preferential vibrational excitation. Pulsed experiments (1-5 kHz) in which gas temperature dynamics are revealed confirm this picture. In pure N_2, vibrational temperatures are observed in excess of 10000K and up to five times higher than the gas temperature. The signature of the Treanor effect (overpopulation of higher levels) is confirmed. These observations are promising in view of economic localized production of fertilizer. Finally, an outlook is given to novel reactor approaches that tailor the plasma dynamics to optimally promote vibrational excitation and to achieve the desired non-equilibrium.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 202A - Session SA+MI-ThM

Ultra-fast Dynamics for Magnetic and Quantum Systems

Moderator: Claus Michael Schneider, Forschungszentrum Juelich GmbH, Germany

8:00am **SA+MI-ThM1 New Opportunities at the APS: Using Intermediate Energy X-rays to Investigate Collective Behavior in Interacting Electron Systems***, **Jessica McChesney**, F. Rodolakis,* Argonne National Laboratory

In an effort to address one of the grand challenges for condensed matter physics in the 21st century, namely to gain an understanding of the physics of materials which exhibit collective electronic phenomena, the Advanced Photon Source has developed the intermediate-energy x-ray (IEX) beamline. Now fully operational, this beamline enables the investigation of collective behavior in interacting electron systems using two distinct but complementary techniques: angle-resolved photoemission spectroscopy and resonant soft x-ray scattering. In this talk, I will discuss some of the unique capabilities of the beamline and present several examples of collective behavior in interacting electron systems including electron-phonon coupling, spin and charge density waves and orbital ordering in high-temperature superconductors, transition metal oxides, topological insulators and heavy fermion materials.

8:20am **SA+MI-ThM2 Observation of Surface Recombination in Ultra-fast Carrier Dynamics of $La_{0.7}Sr_{0.3}MnO_3$ Thin Films***, **Saeed Yousefi Sarraf**, G.B. Cabrera, R. Trappen, N. Mottaghi, S. Kumari, C.-Y. Huang, A. Bristow, M.B. Holcomb,* West Virginia University

Perovskite oxides (ABO_3) are a promising class of transition metal oxides that have attracted significant attention in material science due to diverse range of properties. Many studies on structural and magnetic properties have been done on perovskite oxides to base the multifunctional devices made by and proposed for these materials. Yet another very important property of perovskite oxides is that many of their band gaps are in the visible range. These gaps make these oxides a suitable choice for photovoltaic applications. However, despite the very critical role this property plays in light harvesting devices, there has been a limited understanding about the carrier dynamics of these materials, which inform us about the efficiencies of photovoltaic devices, especially in lower thicknesses. Since by decreasing the film thickness, the surface to bulk ratio increases and surface electrons dominate the bulk electrons, surface recombination might occur as an extra channel of energy relaxation, which decreases the device efficiency. Perovskite oxide $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films were fabricated with different thicknesses by pulsed laser deposition on (100) $SrTiO_3$ single crystal substrates. Our films’ quality were checked by in situ RHEED patterns and oscillations, X-ray diffraction and reflectivity, magnetometry and atomic force microscopy. Ultra-fast carrier dynamics were studied by a degenerate reflectivity pump probe setup at 800nm for different film thicknesses and different pump powers. For films with a thickness above ~20nm three different recombination were observed, attributed to electron phonon relaxation, spin lattice phonon assists relaxation and thermal diffusion relaxation. However, for films thinner than ~20nm an extra relaxation mechanism was observed, which we attributed to surface recombination. This optics work was funded by the American Chemical Society (PRF #56642-ND10); sample growth and optimization were supported by NSF (DMR-1608656).

8:40am **SA+MI-ThM3 Non-equilibrium Control of Charge & Spin Motion in Quantum Materials***, **Hermann Dürr,*** Uppsala University, Sweden **INVITED**

A key driver of modern information technology is the quest for “smaller and faster” information processing and storage. The ultimate speed limit is the speed of light. Therefore, the idea to probe, change and control properties of materials with the help of light has long intrigued researchers in materials science. Of particular interest are magnetic materials which in nanostructured form are used for data storage, memory and processing. In this talk I will show several examples the unique potential of using femtosecond soft x-ray pulses from x-ray free electron lasers such as the LCLS to probe in real time ultrafast spin dynamics in nanoscale systems and during all-optical magnetic switching. Understanding and ultimately engineering the evolving electron, spin and lattice motion on the time- and lengthscales associated with the relevant interactions promises new ways for storing and processing of information.

9:20am **SA+MI-ThM5 XUV-transient Grating: Probing Fundamental Excitations at the Nanoscale***, **Laura Foglia**, F. Capotondi, R. Mincigrucci, D. Naumenko, E. Pedersoli, A. Simoncig, G. Kurdi, M. Manfredda, L. Raimondi,* Elettra-Sincrotrone Trieste, Italy*; N. Mahne,* IOM-CNR, Italy*; M. Zangrando, C. Masciovecchio, F. Bencivenga,* Elettra-Sincrotrone Trieste, Italy **INVITED**

Nonlinear optical spectroscopies take advantage of multiple light-matter interactions via the Nth-order susceptibilities, to disentangle and selectively access the many interacting degrees of freedom that characterize complex systems. Indeed, the control on photon parameters (frequency, arrival time, polarization, etc.) for each field independently gives rise to a manifold of experimental techniques that allow to monitor, on ultrafast timescales, structural changes, spin and electron dynamics, collective phenomena as well as to selectively probe correlations among different excitations. Among the nonlinear processes, third order, or four-wave-mixing (FWM), interactions occur in all materials independently of their symmetry, and are thus the most widely used in applications. While nowadays these techniques are well established at optical wavelengths, their birth required the invention of the laser. Similarly, their extension to sub-optical wavelengths (XUV and X-ray), envisioned theoretically more than a decade ago, had to wait until the recent development of free electron lasers (FELs). XUV-FWM will allow exploiting core-hole resonances to address correlations among low-energy excitations and core states as well as monitoring charge and energy transfer processes. Additionally, it will extend the accessible wavevector range to the mesoscopic regime (0.1-1 nm−1), which is fundamental to investigate, e.g., lattice dynamics in nanostructures and disordered systems as well as transport phenomena at the nanoscale.

Here I report on the demonstration of XUV four-wave-mixing response in a transient grating (TG) approach, exploiting the unique properties of the seeded FEL source FERMI and of two dedicated setups: TIMER and mini-TIMER. All-XUV TG data allowed us to determine the phonon and thermal dynamics of several semiconductors in an uncharted length-scale range, extending down to ≈20 nm. The results are compared with those of XUV pump/optical probe TG, evidencing different couplings to the electronic subsystem.

Additionally, I present the first evidence of FWM processes stimulated by FEL pulses at different wavelengths, obtained exploiting the multi-color capabilities of FERMI and will discuss the foreseen implementation of second order wave-mixing techniques for the chemical and interface specific probing of electronic processes.

11:00am **SA+MI-ThM10 Study of Photo-induced Dynamics in Quantum Materials using Femtosecond Time-resolved X-ray Scattering***, **Wei-Sheng Lee**,* SLAC National Accelerator Laboratory **INVITED**

It remains a great challenge to characterize and understand photo-induced dynamics in quantum materials when it is driven out-of-equilibrium by ultrafast photon pulses. Time-resolved x-ray scattering, enabled by x-ray free electron laser, can track the time-evolution of the magnetic, charge, and lattice degrees of freedom with femtosecond time resolution, providing new insights into the photo-induced dynamics. In this presentation, I will first highlight photo-induced dynamics of spin and charge orders in striped nickelate. The strong coupling between spin and charge orders still survives, despite that both orders have been strongly suppressed by photo-excitations [1,2]. In addition, by resonantly pumping a bond-stretching phonon using mid-IR pulses, we observed lattice-driven dynamics that is different from hot-electron-driven dynamics induced by optical pumping across the band gap [3]. Then, I will discuss phenomena associated with coherent lattice oscillations by highlighting the measurement of atomic displacement of a coherent A1g mode in an iron-based superconductor $BaFe_2As_2$, which can be correlated with accompanied electronic variations [4]. In particular, a quantitative "lock-in" comparison between electronic band structure obtained by time-resolved ARPES and the measured atomic displacements allows us to directly obtain orbital-specific electron-phonon coupling strength without any prior assumption of the electronic band structures [5]. Finally, I will showcase a proof-of-principle time-resolved RIXS experiment on CDW ordered $1T\text{-}TiSe_2$ as an outlook for the future time-resolved x-ray scattering experiment in the next generation x-ray free electron laser, such as the LCLS-II.

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11:40am **SA+MI-ThM12 HAXPES Lab- A Home Lab System for HAXPES Measurements***, S. Eriksson,* Scienta Omicron*; **Anna Regoutz**,* Imperial College London, UK

During the past decade, increased attention has been shown to hard X-rays in the photoelectron spectroscopy field. This is mainly due to the increased information depth enabled by the higher photon energies. Such bulk sensitive measurements could previously only be performed at dedicated synchrotron radiation facilities. The beam lines providing this type of radiation are heavily booked, so access to the experimental setups is thus limited. Higher excitation energies also enables bulk sensitive measurements of deep core levels not accessible with standard XPS.

Here we present a newproduct featuring a monochromized X-ray source giving out Ga Ka radiation at 9.25keV and a wide acceptance angle hemispherical electron analyzer, both combined on a simple to use vacuum system. The base system can easily be customized by adding separate modules such as a MBE- or preparation chamber or a glove box. With this system, a new set of possible experiments opens up in the home laboratory: investigations of buried interfaces, in operando devices, real world samples, etc.

The X-ray source consists of a MetalJet X-ray tube and the electrons which are accelerated into this jet generate an intense Ga Ka radiation. These X-rays are monochromized using a newly developed monochromator. The small spot size of 20 µm provided by the liquid jet source is maintained throughout the passing of the monochromator and only slightly broadened to about 50µm. In order to allow for easy adjustment of the X-ray focal point relative to the electron analyzer, the entire assembly of monochromator and source can be moved down to a precision of a few micrometers. The hemispherical electron analyzer is configured for high kinetic energies allowing for detection of the full energy range the source provides and a large acceptance angle of +/- 30 degrees. The overall system resolution is shown to be <0.5 eV.

We present data taken from polycrystalline gold and silicon wafers with a surface layer of silicon dioxide with a controlled thickness as well as transistor stacks and energy related materials.

Surface Science Division
Room 203C - Session SS+EM+NS-ThM

Defects in and Functionalization of 2D Materials

Moderators: Lars Grabow, University of Houston, Greg Kimmel, Pacific Northwest National Laboratory

8:00am **SS+EM+NS-ThM1 Holes, Pinning Sites and Metallic Wires in Monolayers of 2D Materials***, **Thomas Michely**,* University of Cologne, Germany **INVITED**

The moiré formed by a monolayer of hexagonal boron nitride with Ir(111) provides through a chemisorbed valley region within a physisorbed mesa a unique site for its functionalization. Through gentle ion irradiation and mild annealing a regular array of vacancy clusters is created with the clusters positioned at the valleys where their edges bind to the substrates. Such a nanomesh with a regular array of holes with sizes below 1 nm holds promise for filter applications. Through vapor phase deposition of a variety of materials (e.g. Au or C) arrays of clusters with of tunable size and high thermal stability are formed at valley regions. Compared to the graphene moiré the templating effect of the hexagonal boron nitride moiré is superior due to the uniqueness of the valley pinning site in the unit cell.

Monolayers of hexagonal boron nitride or graphene are also excellent substrates for the on-surface synthesis of new compounds ranging from metal-organic nanowires to transition metal disulfides created by reactive molecular beam epitaxy with elemental sulfur. This synthesis method provides clean, well-decoupled layers with only well-defined defects.

The most exciting defects we observed so far are two types of mirror twin boundaries in MoS_2 islands. In these boundaries we observe for the first time spin-charge separation in real space making use of the unique local spectroscopic capabilities of low temperature STM and STS to identify the position and energy of quantum mechanical states in a one dimensional box. We critically discuss these results in the light of previous related research.

Contributions to this work by Wouter Jolie, Joshua Hall, Clifford Murray, Moritz Will, Phil Valerius, Charlotte Herbig, Carsten Speckmann, Tobias Wekking, Carsten Busse, Fabian Portner, Philipp Weiß, Achim Rosch, Arkady Krasheninnikov, Hannu-Pekka Komsa, Borna Pielić, Marko Kralj, Vasile Caciuc and Nicolae Atodiresei as well as financial support through CRC1238 within projects A01 and B06 of DFG are gratefully acknowledged.

8:40am **SS+EM+NS-ThM3 CO Chemisorption at Pristine, Doped and Defect Sites on Graphene/Ni(111)***, **Mario Rocca**, G. Carraro,* University of Genova, Italy*; M. Smerieri, L. Savio,* IMEM-CNR, UOS Genova, Italy*; E. Celasco, L. Vattuone,* University of Genova, Italy

Due to its electrical properties graphene (G) has been successfully used as a sensing element for the detection of different gases reaching ppm sensitivities which are ascribed to the doping induced by adsorption. The sensitivity depends indeed critically on the chemical nature of the gas and is lower for CO than for other poisoning species. The nature of the active sites is, however, still unclear. If it were due to physisorption, the values of the adsorption energy cannot explain the need for high temperature re-generation of the sensing element. Chemisorption must thus be involved, either at defects or by doping, determining the magnitude of the heat of adsorption and consequently the sensitivity and the range of temperatures at which the sensor can operate. In order to clarify these issues we investigated experimentally adsorption of CO on G supported on polycrystalline Cu and Ni(111) by HREELS and XPS.

No adsorbed CO was found at RT while at 100 K chemisorbed CO forms on G supported on Ni(111). G on Cu is on the contrary inert. This result indicates that the nature of the substrate plays an essential role in the adsorption process. The heat of adsorption q is estimated to be about 0.58 eV/molecule at low coverage, so that an equilibrium coverage of 0.1 ML is expected at RT under a CO partial pressure of only 10 mbar. We identify top-bridge graphene as the most reactive configuration.

Doping G/Ni(111) by N_2^+ ion bombardment allows for the formation of a second, more strongly bound moiety, characterized by a CO stretch frequency of 236 meV and by an initial heat of adsorption (0.85 eV/molecule). The presence of N (in pyridinic or substitutional sites) enhances therefore significantly the chemical reactivity of G/Ni(111) towards CO.

Finally in presence of isolated defects, created by low energy Ne^+ ions bombardment on single layer graphene supported on different substrates (polycrystalline Cu and Ni(111)), no CO adsorption occurs for defected G/Cu, while HREELS peaks form promptly for G/Ni(111). Two moieties, desorbing just above 350 K, are present under vacuum conditions after exposure at RT. The CO stretch frequencies and the ratio of their intensities indicate that they are due to chemisorbed CO at the G/Ni(111) interface close to the vacancies rather than at the defected G layer. The red-shift of the C1s binding energy indicates that in such regions detachment of the G layer from the substrate occurs.

Amending of vacancies occurs for subsequent exposures, as demonstrated by the reduction of the adsorbed coverage in subsequent CO doses followed by annealing at 380 K, indicating that a Bouduard-like reaction takes place under the graphene cover.

9:00am **SS+EM+NS-ThM4 Geometry of Cu Islands Buried Beneath the Surface of Graphite**, *A. Lii-Rosales,* Ames Laboratory and Iowa State University*; S. Julien,* Northeastern University*; Y. Han, J.W. Evans,* Ames Laboratory and Iowa State University*; K.-T. Wan,* Northeastern University*; **Patricia A. Thiel**,* Ames Laboratory and Iowa State University

Deposition of Cu on a sputtered graphite surface, in ultrahigh vacuum, can be manipulated to produce buried islands of metallic, multilayer Cu. The Cu islands are covered by a graphitic layer consisting of several graphene sheets. This layer drapes like a tarpaulin over the Cu islands. We have observed flat-topped islands as tall as 40 nm and as wide as 600 nm. One of the most striking features of island geometry is the fact that the slope of the tarpaulin at the sides of the islands is invariant over a wide range of island volumes. The variation of the ratio of island diameter to height as a function of island volume is far less regular in the experimental data, suggesting that kinetic limitations may play a role in determining this parameter. To investigate the physical forces responsible for the island geometries, we develop a model for island shape that incorporates the distortion energy of graphene, adhesion of Cu with graphitic surfaces, adhesion of graphene with graphite, and other parameters. The energy parameters involving Cu surfaces and Cu-carbon interfaces are derived from DFT calculations. The values and trends predicted by the model are discussed and compared with experiment. In particular, the model indicates that the slope of the island sides should be invariant, consistent with experiment.

9:20am **SS+EM+NS-ThM5 Intercalation of O_2 and CO between Graphene and Ru(0001) and the Role of Defects**, ***Jory Yarmoff**, T. Li,* University of California, Riverside

Graphene (Gr) is a fascinating 2D material that is being widely being considered for applications in electronic devices due to its unique electronic and materials properties. Also, because of its high thermal stability and inertness, it is a promising candidate for use as a protection layer for metal substrates. Here, graphene films grown on Ru(0001) are exposed to O_2 and ^{13}CO and investigated with helium low energy ion scattering (LEIS). LEIS spectra collected at different scattering angles can distinguish between adsorbed and intercalated molecules. It is found that O_2 and CO do not adsorb to the graphene surface but instead intercalate between Gr and the substrate. It is shown that a much lower annealing temperature is needed to remove intercalated oxygen than chemisorbed oxygen on bare Ru. During the thermal desorption, some of the graphene is etched away via chemical reaction forming gaseous CO or CO_2. In addition, carbon vacancy defects are produced in the Gr films via 50 eV Ar^+ bombardment. Isolated single carbon vacancy defects enable molecular adsorption at the defect sites and ease the overall intercalation of oxygen. The defects also improve the thermal etching efficiency of Gr by intercalated oxygen. When the defects are large enough to consist of open areas of bare substrate, oxygen dissociatively chemisorbs to Ru. Intercalated ^{13}CO molecules sit upright with the O end on top, as on clean Ru. The CO molecules tilt, however, when the temperature is raised. This is likely due to increased vibrational amplitudes combined with the confining effect of the Gr film.

9:40am **SS+EM+NS-ThM6 Organic-2D Transition Metal Dichalcogenide van der Waals Heterostructures**, ***Yu Li Huang**,* Institute of Materials Research & Engineering (IMRE), A*STAR, Singapore*; Z. Song,* National University of Singapore*; D. Chi,* Institute of Materials Research & Engineering (IMRE), A*STAR, Singapore*; A.T.S. Wee,* National University of Singapore

The recent emergence of two-dimensional transition metal dichalcogenides (2D TMDs) has led to a rapid burgeoning of the field due to their novel electronic and optical properties with potential electronics/photonics applications. Organic materials, on the other hand, have exhibited great success in the field of flexible electronics, with an extensive number of available molecules with tunable properties. Marrying the fields of organics and 2D TMDs will bring benefits that are not present in either material alone, enabling even better, multifunctional flexible devices. In parallel, the integration of 2D TMDs with selected organics is also a promising and controllable approach to modulate the properties of the TMDs without structural damage, thereby optimizing or even enhancing their desired properties for specific device applications. Central to the realization of all those applications is a fundamental understanding of the organic-2D TMD interface.[1]

Here, we will present our recent studies on hybrid organic/2D TMD heterostructures.[2-4] With combined experiments and theoretical modeling, the interfacial interactions between the organic layers and the TMDs as well as the energy level alignment at the interface are explored. The comprehensive understanding of the underlying physical mechanisms that govern the properties of organic-2D TMD interfaces at the atomic scale is of fundamental importance for developing this technique further for device applications.

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11:00am **SS+EM+NS-ThM10 Influence of Surface Functionalization on Surface Topography and Growth of Metal Oxide Structures on HOPG**, ***Kathryn Perrine**, M. Trought, I. Wentworth, C. de Alwis, T.R. Leftwich,* Michigan Technological University

Growth of heterogeneous catalysts, plasmonic and other nanostructured materials requires atomic level control and molecular level understanding of the growth of metals and metal oxides on surfaces. Surface functionalization of 2D materials can be used to promote selective nucleation of metal oxides with control over the deposition and growth. However, this requires an understanding of surface functionalization. This surface chemical functionalization can be combined with the atomic-level control of atomic layer deposition (ALD). ALD is a vapor deposition technique that utilizes self-limiting surface reactions to grow metal oxides, where the surface functional group initiates the first step in the deposition process.

2D materials are ideal for selective functionalization that may not require lithography steps due to the fact that their sheets are in a stable configuration making them chemically unreactive. Highly oriented pyrolytic graphite (HOPG) is an ideal model of the graphene surface, a well-known 2D material, which is comprised of sp^2 hybridized aromatic hydrocarbon sheets. HOPG consists of stacked graphene sheets where the terraces of the carbon sheets are chemically unreactive in ambient conditions and their defects are highly reactive. Oxidation methods are used to produce an assortment of different functional groups on HOPG and can lead to different types of functionalities on the surface and its defects.

We investigate how surface oxidative etching and functionalization influences the growth of metal oxide structures at tailored defects and functional sites on HOPG. Two different acids were used to etch the HOPG surface to produce functional groups resulting in different surface topographies. The functionalized HOPG was then exposed to trimethylaluminum and water, a well-known ALD reaction, to produce Al_2O_3 as a proof-of-concept to observe the growth of Al_2O_3 on both functional and defect sites. Vibrational spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were used to measure surface functionalization and Al_2O_3 growth on HOPG. Field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and Raman spectral imaging were used to image the changes in surface topography after etching and ALD deposition. Results indicate that the Al_2O_3 deposition and growth is dictated by the surface functionalization and topography. This suggests that understanding the effects of surface functionalization of 2D materials is necessary for controlling the growth of metal oxide structures.

11:20am **SS+EM+NS-ThM11 Impurity Induced Chemical Properties of BN on Rh(111) Studied by First Principle Calculations: A New Phase**, ***Zahra Hooshmand***[1], *D. Le, T.S. Rahman,* University of Central Florida

Hexagonal boron nitride (h-BN), an insulating layer of sp^2 hybridized structure between B and N, grown on Rh(111) forms a Moiré pattern with elevated (rim) and depression (valley) areas. The valleys are circular dipole rings which act as trapping centers for the adsorption of nanoparticles and molecules [1]. The presence of the native carbon impurities in Rh potentially gives rise to the formation of hexagonal carbon rings under every other rim area as suggested by recent experiments [2] and could lead to new structures and novel chemistry. Here, on the basis of Density Functional Theory (DFT) simulations with dispersion corrections, we show that these rings tend to grow in a manner in which the center of each ring is placed on top of the Rh atom. These rings grow next to each other and form islands which are separated from each other by an equal distance while the BN monolayer remains untouched, i.e. there is no C-B or C-N bond formed. Our calculations show that while no broken bonds between B and N were observed, the increase in the concentration of carbon impurities will enhance the height modulations among different regions of BN Moiré pattern leaving the former valleys unchanged while decreasing their area. The new higher elevated regions show strong accumulation of charge and the lower elevated regions display depletion of charge. This gives rise to modification of dipole rings and results in altered adsorption of pentacene on BN. Our simulations of Scanning Tunneling Microscope (STM) images from this structure, are in good agreement with experimental data for number of rings from 3 to 5. However spatial density of states analysis shows that in the presence of 5 rings islands the gap in BN on the higher elevated regions vanishes and the band gap on these areas for 3 and 4 rings islands reduces. The calculations of local variations in work function also show that these variations become more pronounced by growth of islands and reduces the work function of lower elevated regions in new phase. This results show that by control of the concentration of local impurities underneath the rim areas in BN, the chemical properties are modified and the monolayer could be engineered for interesting chemical reactions. [1] H. Dil et al., *Science*, 2008, 319, 1824-1826. [2] Koslowski et al. Private communication.

This work was supported by National Science Foundation, Grant #NSF CHE-1465105"

11:40am **SS+EM+NS-ThM12 Texture of Atomic-layer Deposited MoS: A polarized Raman Study**, ***Vincent Vandalon***, *A. Sharma, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands*; A.A. Bol,* Eindhoven University of Technology, Netherlands

Advances in optical characterization techniques for 2D transition metal dichalcogenides (2D-TMDs) such as MoS2 are essential in the context of tailoring the texture and surface functionalization of these materials. Tailoring of the texture of *synthesized* MoS2 results in uniquely different material characteristics: out-of-plane fins of MoS2 have been demonstrated to possess excellent catalytic performance, most likely due to exposed catalytically active edge sites, whereas basal plane oriented MoS2 shows excellent electronic properties. The large impact of texture on the exhibited properties underlines the need for rapid and facile characterization of the texture and especially the angular grain orientation. So far, cross section high-resolution transmission electron microscopy (HR-TEM) is widely employed to obtain insight into texture but it suffers from a limited throughput. On the other hand, Raman spectroscopy has been established as the *go-to* technique for the determination of e.g. film thickness of these TMDs. Here we will show that the angular grain distribution can also be determined using *polarized* Raman spectroscopy

We have found that plasma-enhanced atomic-layer deposition (PE-ALD) of MoS2 allows control over the texture and results in out-of-plane fins or basal plane oriented material depending on the processing conditions using HR-TEM. To study the texture of the PE-ALD synthesized films with Raman spectroscopy, we have investigated the so far unknown impact of the angular grain distribution on the Raman response. The Raman response of nanocrystalline MoS2 was modeled for a range of different textures. This allowed us to determine the angular grain distribution from the peak ratio of the two dominant Raman peaks (i.e. the A1g and E2g modes). Furthermore, the modeling also showed that performing *polarized* variant of Raman spectroscopy is essential for the accurate determination of the angular grain distribution because of the additional information it provides. A systematic polarized Raman study into the evolution of the fraction of out-of-plane material with film thickness allowed us to gain insight into the growth process. Moreover, the influence of a post-deposition high-temperature anneal in a H2S atmosphere on the texture, known to yield improved material properties, was also investigated. To conclude, polarized Raman spectroscopy offers a rapid method to gain insight into the angular grain distribution of synthesized MoS2 and this approach can be readily extended to other MX2 materials.

Thin Films Division
Room 102A - Session TF+AS+EL+PS-ThM
In-situ Characterization and Modeling of Thin Film Processes

Moderator: Thomas Riedl, University of Wuppertal

8:00am **TF+AS+EL+PS-ThM1 Defects in Thin Films: A First Principles Perspective**, ***Douglas Irving***, *J.S. Harris, J.N. Baker, S. Washiyama, M.H. Breckenridge,* North Carolina State University*; P. Reddy,* Adroit Materials*; R. Collazo, Z. Sitar,* North Carolina State University **INVITED**

Realization of next-generation power and optoelectronic devices depends on the ability to controllably donor dope thin films of AlN and Al-rich AlGaN. The challenge in donor doping these materials begins with the donor dopant itself, Silicon. While it is a common shallow donor dopant in GaN, it exhibits a deeper ionization level in AlN due to the formation of a DX center near the conduction band minimum. Compensation in both the low and the high doping regime also presents a significant technical challenge to the doping of AlN thin films. In this talk, we explore the mechanisms for compensation in Si-doped AlN in the low and high doping regimes. For this purpose, we have implemented first principles density functional theory calculations with screened hybrid exchange-correlation functionals to determine the properties of individual defects in AlN. The formation energies of each defect are used within a grand canonical equilibrium model to identify the predominant defects as a function of growth conditions. In the low doing regime, important to drift layers in power electronics, we find unintentional impurities and unintentional impurity complexes are often responsible for free carrier compensation. Compensation in films that are doped to higher impurity concentration is found to be related to vacancy-dopant complexes. Possible solutions unique to thin films have also been explored and will be presented. Results from these methods are compared with complementary experimental data that includes below band gap optical absorption and photoluminescence, electrical measurements, dopant implantation, and available SIMS measurements.

8:40am **TF+AS+EL+PS-ThM3 Advances in Numerical Simulation of SiN ALD**, ***Paul Moroz,*** TEL Technology Center, America, LLC

Atomic layer deposition (ALD) includes a fast growing area of applications and could be foreseen as becoming one of the leading semiconductor technologies. In many cases, it allows accurate atomic-scale deposition of films with almost conformal profiles. Here we present new results on the Monte Carlo feature-scale simulations of ALD conducted with a feature-profile simulator, FPS3D [1-5], as well as comparison of obtained simulation results with the corresponding experiments. The ALD processes are often complex, involving large molecules and, to our knowledge, have not been addressed by other feature-profile simulations except FPS3D. The main factor of all of ALD schemes is the cyclic change in flux parameters and in the corresponding surface chemistry, which results in a single monolayer or, most typically, in a fraction of a monolayer of a film deposited after application of a cycle. Here, we consider a case of ALD with two time-steps:

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[1] **National Student Award Finalist**

(1) dichlorosilane gas and (2) ammonia plasma. The SiN deposition rate in this case is about a half of a monolayer per cycle. A set of surface reactions is considered which emphasize the steric hindrance effect that was found to be an important factor in explaining deposition rates for this ALD process.

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9:00am **TF+AS+EL+PS-ThM4 Diffusion Kinetics Study of Adatom Islands: Activation Energy Barriers Predicted using Data-driven Approaches***, **ShreeRam Acharya**, T.S. Rahman,* University of Central Florida

The Self-Learning Kinetic Monte Carlo (SLKMC) method [1] with a pattern recognition [2] and a diffusion path finder scheme enables collection of a large database of diffusion processes including single- and multiple-atoms, and concerted island motion and their energetics. The databases collected from adatom-island (2-8 atoms) diffusion characteristics for a large set of homo- and hetero-epitaxial metallic systems (Cu, Ni, Pd and Ag) are used to extract a set of easily accessible features, geometrical and energetic, using physical insight which are then encoded. Those features along with activation energy barrier are used to train and test linear and non-linear statistical models. A non-linear model developed based on neural network technique predicts the diffusion energy barriers with high correlation with the calculated ones. In this talk, we present the results of kinetics study of these homo or hetero-epitaxial metallic systems some of whose barriers are used for training of the model and are compared to the corresponding quantities obtained from KMC simulation using energy barriers calculated from computationally intensive interatomic interaction potential based approach.

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Work supported in part by MMN-1710306.

9:20am **TF+AS+EL+PS-ThM5 Using Ellipsometry and XPS to Understand the Degradation of Thin-film Aluminum Mirrors Protected by Ultrathin Fluorides***, M.R. Linford, **Brian I. Johnson**, R.S. Turley, D.D. Allred,* Brigham Young University

The LUVOIR (Large, UV-optical-IR) telescope is a potential NASA flagship space-based observatory of the 2020's or 30's. It will utilize the largest mirrors ever put into space. The reflective coating for the mirrors will be aluminum, since there is no material with comparable reflectance at shorter wavelengths. However, to achieve high reflectance over the broadest energy range, the top surfaces of such Al mirrors must be protected against the formation of oxide layers that form quickly in air using wide-bandgap fluoride coatings, traditionally about 25 nm of MgF_2. Researchers have been endeavoring to use fluorides which are transparent further into the VUV (vacuum ultraviolet) like LiF and AlF_3, and to make these barriers more continuous by depositing them on heated surfaces and making the barriers thinner. However, when the barriers are thinner and when materials like LiF are exposed to moist air, degradation of VUV reflectance is observed. Thus, studying fluoride barrier-coated mirrors is vital. We have recently reported on the time dependent growth of apparent aluminum oxide thickness for two Al mirrors protected by ultrathin fluoride layers. These measurements were based on variable-angle, spectroscopic ellipsometric (VASE) measurements. (Allred, Thomas, Willett, Greenburg, & Perry, 2017) (Miles, 2017) . VASE, however, does not provide chemical composition data. An independent analytical technique which is sensitive to surface composition is required. We have undertaken such investigations using X-ray photoelectron spectroscopy (XPS), and now report on correlations between optical properties and XPS for fluoride-coated aluminum mirror test structures.

9:40am **TF+AS+EL+PS-ThM6 Model for Amorphous Thin Film Formation and Validation***, **Rahul Basu**,* VTU, India

A coupled set of equations describing heat and mass transfer during phase transformation is formulated The model is extended to incorporate surface convective effects. These equations which are non linear due to the moving interface are linearized and decoupled. Effects of various heat transfer parameters are analyzed through small parameter expansions. Solutions obtained via this artifice allow closer examination of surface effects on the boundary layer of the phase transformation. A relation is found for the effect of the glass transition temperature versus the boundary layer thickness for several alloys in various groups of the Periodic Table. Earlier work and results are analyzed in light of the present analysis.

11:00am **TF+AS+EL+PS-ThM10 2D TMD Monolayer of MoS_2 BY ALD and Insight in the Mechanism by Surface Organometallic Chemistry***, **Elsje Alessandra Quadrelli**,* CNRS CPE Lyon, France **INVITED**

Atomically-thin crystalline domains of MoS_2 [1] or WS_2 [2] are obtained from an organometallic amorphous deposit obtained by ALD/MLD.

This original result with respect to the state of the art has been mechanistically rationalized with in situ and in operando modelling studies on the oxide nanobeads at different annealing temperatures. This contribution will present the surface organometallic method, the characterization of the 2D layers (among which the first in-plane micrographs of ALD-grown MoS_2 samples)[1] and the proposed surface coordination chemistry mechanism at hand obtained with model studied on 3D silica beads. These model studies couple in operando infra-red spectroscopy, gas-chromatography detection of the released by-products and atomic composition of the deposit at each cycle, leading to molecular level understanding of the growth process.

***Acknowledgments** : This work was carried out within the framework of the partnership between the C2P2 research unit (UMR 5265 CNRS CPE Lyon University Claude Bernard Lyon 1) and CEA's Directorate of Technological Research (DRT) on the nanochemistry platform installed in CPE Lyon. The authors of the papers below thank CPE Lyon, CNRS, CEA / LETI (Silicon Technology Department and nanocharacterization platform) for the support and the DRF / INAC for the collaboration in the framework of the "2D Factory" project.*

***Ref** : [1] Cadot et al.Nanoscale , **2017**, 9, 467. [2] Cadot et al. JSVT A **2017**, 35, 061502 .*

11:40am **TF+AS+EL+PS-ThM12 A Novel Fourier Transform Ion Trap Mass Spectrometer for Semiconductor Processes***, **Gennady Fedosenko**, H.-Y. Chung, R. Reuter, A. Laue, V. Derpmann, L. Gorkhover, M. Aliman, M. Antoni,* Carl Zeiss SMT GmbH, Germany

Real-time inline control of process gas compositions with high sensitivity has been of particular importance in recent years in the semiconductor industry and beyond. Commonly quadrupole residual gas analyzers (RGA) are used, together with Optical Emission Spectroscopy (OES) for process control and process development. However, most RGAs are not capable of measuring a whole mass spectrum fast enough to monitor etch or deposition processes of a few seconds. A new process control mass spectrometer, based on Fourier-Transform 3D Quadrupole Ion Trap technology, is more appropriate for real-time inline process monitoring.

The 3D-Quadrupole Ion Trap mass spectrometer *iTrap*® by ZEISS is installed in a vacuum chamber (~ 120mm x 120mm x 500mm) with a fast switching valve for pulsed gas sample injection (pulse duration ~ 50ms or less). An electron gun is used for ionization of the gas pules. The Ion Trap achieves ion trapping and accumulation by means of a radio frequency applied to the ring electrode of the trap. With the aid of advanced electronic amplifiers and selective ion excitation technique the ion oscillations can be measured electrically by means of the induced current on the cap electrodes without using any separate particle detector. The mass spectrum can be finally obtained in less than one second.

Real-time measurements of the hydrogen plasma cleaning process of Sn contaminated samples were performed with the *iTrap* mass spectrometer. The working pressure of the plasma cleaning process was 0.5 mbar. Decreasing signal of SnH_4 and other contaminations from the samples which are directly correlated to the cleaning process were observed with *iTrap*. This result is extremely useful for the process control of plasma processes and inline real-time contaminations control for high-end applications.

Inline measurement at a MOCVD chamber showed that *iTrap* is capable to detect reaction products, contaminations on the wafer holder and dopant memory in real-time. These results demonstrate that *iTrap* is a very sensitive and fast process mass spectrometer suitable for real-time inline process monitoring.

Many etch processes take place in 10 to 30 s process steps. Different processes were examined with e.g. HBr or BCl_3 chemistry together with several wafer materials such as Silicon, Hafnium Oxide or Titanium Nitride. The obtained mass spectra show the etch plasma chemistry together with etch reaction products (HfClx, SiClx, etc.). This data gives new insight into the etch processes, which until now were rarely understood on a chemical level. First wafer effects related to the chamber cleaning and pre-coating steps prior to the etch step were also examined.

12:00pm **TF+AS+EL+PS-ThM13 Realization of Shifts in Threshold Voltage and Subthreshold Swing in Atomic Layer Deposited Zinc Oxide As Channel Layer through *in-situ* Half-Cycle Analysis*, Harrison Sejoon Kim*,** *A.T. Lucero, S.J. Kim, J. Kim,* University of Texas at Dallas

Thin film process monitoring of atomic layer deposition (ALD) has been adopted as the versatile technique to identify both chemical and physical properties of ALD films. Their *in-situ* characterization technique includes mostly Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and quartz crystal microbalance analysis. [1–3] However, currently there are no reports on monitoring the results of sub-nm device physics even if we are already in the era of beyond 10 nm node semiconductor processes. Moreover, even if there are a few initial studies, demonstrating *in-situ* electrical characterization with ALD, it requires device packaging, which ultimately limits the flexibility to be further characterized. [4]

In this current work, we have developed an ultra-high vacuum (UHV) cluster tool equipped with thermal processing, plasma surface treatment, thin film deposition, and electrical characterization which can be performed *in-situ* (Figure 1). With this feasibility, we demonstrate the deposition of semiconducting zinc oxide (ZnO) in inverted-coplanar structured thin film transistors (TFT). Diethylzinc (DEZ) and water (H_2O) is used as ALD precursors at 100°C. DEZ and H_2O half-cycle analysis is carried out to monitor the interface states of ZnO/dielectric (Figure 2). Initially, 45 ALD cycles of ZnO have shown switching behavior with an on/off ratio of ~10^2 in vacuum. Subsequent ALD cycle shifts the threshold voltage (V_{th}). V_{th} shifts associated with each ALD cycle are assumed to be attributed to the changes in interface trap density as a result of interface state passivation in ZnO during its growth, especially passivating fixed oxide charges (Q_{ox}). To understand interface states of ZnO and the bulk of oxide better, further analysis of shift of subthreshold swing (SS) is demonstrated. Since shifts in SS best represents changes in interface trap density, [5] it is worthwhile to note the changes in SS in metal-oxide-semiconductor transistors.

This work was supported by the Creative Materials Discovery Program on Creative Multilevel Research Center (2015M3D1A1068061) through the National Research Foundation(NRF) of Korea funded by the Ministry of Science, ICT & Future Planning.

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[3] C. L. Hinkle *et al*., *Appl. Phys. Lett.91*, 1, **2007**.

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Thin Films Division
Room 104B - Session TF+PS-ThM
Deposition Processes for 3D and Extreme Geometries

Moderators: Richard Vanfleet, Brigham Young University, AnnaMaria Coclite, Graz University of Technology

8:00am **TF+PS-ThM1 ALD and Diffusion in High Aspect Ratio Carbon Nanotube Forests*, David Kane,*** *R.C. Davis, R.R. Vanfleet,* Brigham Young University

Very high aspect ratio or nanostructured materials have numerous applications. In many of those applications, the surface is decorated by atomic layer deposition or other vapor phase deposition techniques. In these extreme geometries the uniformity of deposition is a function of the interplay between transport (diffusion) and reaction rates. The A-B cycling in Atomic Layer Deposition (ALD) separates the deposition reaction from the transport. We have observed a limited penetration depth which decreases with cycle number in ALD on vertically aligned multiwall carbon nanotube (MWCNT) forests with an effective aspect ratio of 1000. Models of ALD in high aspect ratio features based on Knudsen diffusion transport combined with a simple geometric model of nucleation and growth on surfaces with a low nucleation site density can qualitatively reproduce the observed deposition. Fitting the models to the data allows extraction of the diffusion coefficients for these confined geometries.

8:20am **TF+PS-ThM2 Nanoporous Reference Substrates for ALD on High Aspect Ratio High Surface Area Materials*, Dmitri Routkevitch,*** InRedox

Deposition of conformal and uniform coatings onto high aspect ratio high surface area substrates and materials is a unique domain of ALD impacting many important applications, including energy generation and storage, semiconductor device manufacturing, chemical and biosensing and many others. However, ALD process development on such substrates is hindered by complex material geometry leading to poorly understood transport conditions and high cost of real substrates, such as large Si wafers at later staged of processing. In addition, modern ALD reactors, designed and optimized for high speed processing of flat substrates, require validation of uniformity and conformality of ALD coatings both inside the pores and laterally across the high surface area substrates with complex multiscale topology.

<u>Nanoporous Anodic Aluminum Oxide (AAO)</u> – a self-organized material resembling nanoscale honeycomb – is a controllable, well-defined, inexpensive and convenient nanomaterial platform to support the development and validation of high surface area ALD. The combination of ALD with AAO enables control of both the nanoscale geometry and chemistry with unprecedented precision to provide new avenues for design and engineering of functional materials and devices.

Some of the benefits of AAO as a reference ALD substrate are:

1. Highly uniform and parallel cylindrical pores, complex pore structures (modulated, branched, etc) available to emulate different pore size distributions of other materials.
2. A broad spectrum of transport conditions (pore diameters from 2 nm to 500 nm and pore lengths from <100 nm to >300 µm for aspect ratio (L/D) from 1 to as high as 50,000) that could be tested to aid better understanding and rapid development of new ALD processes.
3. Reproducible and well-understood surface chemistry of alumina makes it nearly universally suitable for many binary reactions involved in ALD.
4. High pore densities (10^{12} to 10^7 cm^{-2}) allow straightforward characterization of elemental depth profiles by EDS even for very thin (5-10 nm) coatings.
5. Available in different form factors and on different substrates (flexible foils and tapes, rigid plates, Si wafers, glass blanks, etc) to accommodate different types of ALD reactors, such reel-to-reel reactors for coating battery electrodes or reactors designed to process stacks of Si wafers or PV substrates.

Scaleable to large sizes, low cost.

Several case studies will be presented where AAO was used as a reference substrate to aid the development of ALD for high surface area materials.

8:40am **TF+PS-ThM3 Fine-tuned Resistive Coatings for Detector Applications*, Maximilian Gebhard,*** *A.U. Mane, D. Choudhury, S. Letourneau, D.J. Mandia, Y. Zhang, J.W. Elam,* Argonne National Laboratory

An important building block for detector devices are amplifiers, such as microchannel plates (MCPs). Due to the geometry of several periodically arranged microchannels, incident electrons or irradiation can be amplified by several orders of magnitude, making MCPs highly efficient in several applications such as neutron detectors and night-goggles. The efficiency of state-of-the-art MCPs is strongly related to functional coatings, acting as resistive coating and secondary electron emission (SEE) layer. While the SEE material (*e.g.* Al_2O_3 or MgO) should exhibit a high SEE coefficient, the resistive coating must facilitate a uniform and stable electrostatic field along the pores and during operation. It was shown previously that atomic layer deposition (ALD) is capable to produce highly efficient SEE coatings (MgO) as well as a fine-tuned resistive coating directly on the MCP substrate, thereby improving the overall performance of the detector devices.[1,2] By producing highly conformal thin films over large areas and on large aspect ratios, ALD is the method of choice to produce functionalized MCPs.

One challenge in manufacturing reliable MCPs for advanced applications are external conditions like ambient temperature. With temperature gradients of 100 K or higher, the thermal coefficient of resistance (TCR) of the resistive coating plays a major role with respect to electrical transport phenomena. Positive TCRs can cause increased resistance at elevated temperatures and in due turn a collapse of the MCP's performance. Similar determining factors are on hand for strongly decreased temperatures. A second challenge is the fluorine-based chemistry, which is currently often employed to produce ALD-functionalized MCP coatings.

We present here the development of ALD-fabricated materials, being free of fluorine chemistry and exhibiting tailored electric resistance over a broad temperature range as well as promising performance as resistive coating in MCPs. Apart from thorough process development, those transition metal-based materials were analyzed regarding their composition, structure and electrical behavior employing XPS, SEM, XRD and extended IV-measurements. Furthermore, the coatings were applied to MCPs, which were tested for their performance.

[1] A. U. Mane and J. W. Elam, *Chem. Vap. Deposition*, **2013** (19), 186-193

[2] M. J. Minot, B. W. Adams, M. Aviles, J. L. Bond, C. A. Craven, T. Cremer, M. R. Foley, A. Lyashenko, M. A. Popecki, M. E. Stochaj, W. A. Worstell, A. U. Mane, J. W. Elam, O. H. W. Siegmund, C. Ertley, H. Frisch and A. Elagin, *Proceedings Volume 9968, Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XVIII*, **2016**, DOI: 10.1117/12.2237331

9:00am **TF+PS-ThM4 Tungsten Atomic Layer Deposition on Vertically Aligned Carbon Nanotube Structures***, **Ryan Vanfleet**, R.C. Davis, D.D. Allred, R.R. Vanfleet,* Brigham Young University

Carbon Nanotubes (CNTs) can be grown from 2D patterns into high aspect ratio, 3D MEMS structures. These porous structures can then be filled solid with different materials in order to impart specific and unique properties to the MEMS device. Tungsten, with its conductivity, high density and high temperature resistance, could be of special interest for many MEMs devices. Due to the high packing density and high aspect ratios of vertically aligned CNT forests, it is difficult to uniformly deposit films throughout the entirety of the structure. Atomic Layer Deposition (ALD) has been shown to uniformly coat structures with extreme geometries using sequential, self-limiting surface reactions. This in an inherently slow process, especially on geometries where the deposition is diffusion-limited such as in CNT forests. Approximately 50 nm of tungsten is required to fill a CNT-patterned structure solid where the individual CNTs grow roughly 100 nm apart. The tungsten ALD process has been shown to be able to deposit more than a single atomic layer per cycle so that the necessary number of cycles to fill the CNT structure is reduced. The process parameters that facilitate this increased deposition rate will be discussed. Tungsten-filled CNT beams were subjected to three-point bending tests to determine material properties of the composite structures. Preliminary tests on beams with about 35 nm of as-deposited tungsten give an ultimate strength of 11 MPa and a Young's Modulus of 1.7 GPa. The microstructure of the as-deposited tungsten is extremely fine and annealing studies will also be addressed.

9:20am **TF+PS-ThM5 ALD in Metal Organic Frameworks: Toward Single Site Synthesis and Sinter-Resistant Catalysts***, **Alex Martinson**,* Argonne National Laboratory **INVITED**

Reproducibly and homogeneously synthesizing single-site transition metal catalysts on exceedingly high surface area supports with stability under catalytic conditions remains a grand challenge. To address this challenge, we utilize atomic layer deposition (ALD) in metal-organic frameworks (MOFs), a process we call AIM. Here, ALD provides a straightforward gas phase route to access a wide variety of small precision clusters with spatial and dimensional homogeneity. The well-defined structure of MOF NU-1000 framework and nodes allows for detailed characterization of their size and uniforming as well as insight into their inherent stability. This talk will discuss several classes of ALD precursors and processing conditions that have been identified to be compatible with few-atom cluster deposition in Zr-based MOF NU-1000.

11:00am **TF+PS-ThM10 Alumina Deposition by Atomic Layer Deposition (ALD) on Flat Surfaces and High Aspect Ratio Structures***, **Dhruv Shah**, D.I. Patel, D.J. Jacobsen, J.E. Erickson, M.R. Linford,* Brigham Young University

Atomic layer deposition (ALD) involves layer-by-layer deposition due to sequential exposure of two precursors to as substrate . ALD was developed in the late 1970s by Suntola and co-workers as a modification of chemical vapor deposition (CVD). In ALD, the dosing and purging steps are separated to ensure that each precursor saturates the surface before the other precursor enters the chemical reactor. ALD is widely used in the semiconductor and microelectronics industry to deposit thin films of various oxides on different substrates. ALD can be operated in two modes: plasma assisted and thermally assisted. Thermally assisted ALD has been widely used due to its high uniformity and conformality in depositing thin films on a variety of substrates.

Here we report alumina deposition by ALD using trimethylaluminum and water as precursors on silicon substrates. We optimized the process on flat surfaces like silicon shards, and extrapolate the process to high aspect ratio devices and powders, ultimately confirming the deposition on these high aspect ratio materials. Achieving high degrees of consistency and uniformity for deposition on powders through a frit using ALD has been difficult. We tried multiple recipes for alumina deposition, optimizing the dose time, purge time and effective exposure of the precursor on the substrate to achieve uniform results. Our thin films are characterized by spectroscopic ellipsometry (SE), water contact angle goniometry, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and/or transmission electron microscopy (TEM). The thin films we have obtained on planar substrates using ALD vary in thickness from 0.5 – 41.0 nm. These thin films were used to conduct a multiple sample analysis (MSA) in SE to obtain the optical constants of alumina. Since alumina is one of the most commonly used material in microfabrication, its optical constants will be useful in the field.

11:20am **TF+PS-ThM11 Resistivity of the Alumina Diffusion Barrier in Catalytic Carbon Nanotube Growth***, **Berg Dodson**, G. Chen, R.C. Davis, R.R. Vanfleet,* Brigham Young University

By using photolithography techniques and catalytically grown carbon nanotubes (CNTs) it is possible to fabricate high aspect ratio structures that can be used as scaffolds for MEMS devices. The drawback of making CNT structures this way is it is difficult to electrically connect to them since they are grown on an insulating alumina layer. However, previous work demonstrates that the alumina layer becomes conductive during CNT growth. Two-point probe measurements from tungsten to a CNT post in a 100 nm tungsten/alumina 50 nm/CNT stack yielded 580 ± 65 Ω. I present TEM based data showing how this change in conductivity correlates with iron and carbon diffusing into the alumina layer during CNT growth. I will also show how the observed diffusion in these samples compares with what is predicted by diffusion models as well as how the change in resistivity compares to what is expected in doped alumina.

11:40am **TF+PS-ThM12 High Temperature Active CeO_2 Nanorods Generated via Diffusion Limited Atomic Layer Deposition***, **Haoming Yan**, X.Z. Yu, Q. Peng,* University of Alabama

CeO_2 has attracted lots of attention due to its superior oxygen storage and donating ability as a catalyst support. CeO_2 nanorods has the best donating ability than all the other types of CeO_2 materials. However, the nanorods change its morphology and lose its activity at 400°C or above. Therefore, improving the thermal stability of CeO_2 nanorods can unlock the potential applications of CeO_2 nanorods in the high temperature applications. In this work, we introduce a diffusion-limited Al_2O_3 atomic layer deposition to selectively passivate the surface site of CeO_2 nanorods, largely enhancing its thermal stability and its oxygen storage capacity simultaneously.

2D Materials Focus Topic
Room 201B - Session 2D+EM+MN+NS-ThA

Novel Quantum Phenomena in 2D Materials

Moderator: Hsin Lin, Institute of Physics, Academia Sinica

2:20pm **2D+EM+MN+NS-ThA1 Double Indirect Interlayer Exciton in a $MoSe_2$/WSe_2 van der Waals Heterostructure**, ***Aubrey Hanbicki***, *H.-J. Chuang, M. Rosenberger, C.S. Hellberg, S.V. Sivaram, K.M. McCreary, I. Mazin, B.T. Jonker,* Naval Research Laboratory

Tailoring semiconductor heterostructures for specific functionalities has led to varied opto-electronic devices including solar cells, photodetectors, light-emitting diodes and lasers. An emerging class of heterostructures involves monolayer semiconductors such as many of the transition metal dichalcogenides (TMDs) which can be combined to form van der Waals heterostructures (vdWHs). vdWHs offer novel functionalities making them promising hosts for future devices. One unique new heterostructure property is an interlayer exciton (ILE), a spatially indirect, bound electron-hole pair with the electron in one TMD layer and the hole in the other. Here, using state-of-the-art preparation techniques, we are able to resolve emission from the ILE in a $MoSe_2$/WSe_2 heterostructure into two distinct peaks separated by 24 meV at zero field. These peaks have nearly equal intensity, indicating they are of common character, and have *opposite* circular polarizations when excited with circularly polarized light. *Ab initio* calculations successfully account for these observations – they show that both emission features originate from excitonic transitions that are indirect in momentum space and are split by spin-orbit coupling. Also, the electron is strongly hybridized between both the $MoSe_2$ and WSe_2 layers, with significant weight in both layers, contrary to the commonly assumed model. Thus, the transitions are not purely interlayer in character. This work represents a significant advance in our understanding of the static and dynamic properties of TMD heterostructures.

This research was performed while H.-J.C. held an American Society for Engineering Education fellowship and M.R.R and S.V.S held a National Research Council fellowship at NRL. This work was supported by core programs at NRL and the NRL Nanoscience Institute. This work was also supported in part by a grant of computer time from the DoD High Performance Computing Modernization Program at the U.S. Army Research Laboratory Supercomputing Resource Center.

2:40pm **2D+EM+MN+NS-ThA2 Comparison of A- and B-exciton Intensity and Polarization in Transition Metal Dichalcogenide Monolayers and Heterostructures**, ***Kathleen McCreary***, *A.T. Hanbicki, S.V. Sivaram, B.T. Jonker,* U.S. Naval Research Laboratory

We survey a large number of monolayer TMDs to better understand the conditions responsible for various emission characteristics that have been reported in literature. We find that the intensities for both A- and B- peak emission vary widely as a result of sample-to-sample variations. However, a measurable B-peak intensity is evident in all samples. There is a clear linear relationship between the two peak intensities. The emission from the dominant A-peak is commonly several orders of magnitude higher than B-peak emission, resulting in B/A-intensity ratios well below 1%. Yet, as the A-peak intensity decreases, the ratio of B/A monotonically increases, and we observe a B/A ratio up to 30% in monolayer MoS_2. The A-excitonic emission is further quenched when $MoS_2$is incorporated into an MoS_2/$MoSe_2$heterostructure, where we observe comparable A- and B-peak intensities. We attribute these variations to differences in exciton recombination times, clarifying contradictory reports regarding the accessibility and significance of B-peak emission. Furthermore, we observe a high degree of valley polarization in both B-exciton emission in isolated monolayers and A-exciton emission in heterostructures, consistent with our model detailing the rapid exciton lifetimes in B-emission and van der Waals heterostructures.

Supported by core programs at NRL and the NRL Nanoscience Institute

3:00pm **2D+EM+MN+NS-ThA3 Optospintronics and Magnetism with 2D Materials and Heterostructures**, ***Roland Kawakami,*** The Ohio State University **INVITED**

I will review our latest developments in spintronics, optospintronics and magnetism in two-dimensional (2D) materials and heterostructures. Graphene continues to exhibit improved properties for spin transport and demonstrates additional functionality through the use of vertically stacked heterostructures. One of the interesting new directions is optospintronics enabled by heterostructures of graphene and transition metal dichalcogenides (TMD) [1]. Due to the valley optical selection rules of TMDs and the large spin-orbit coupling, the helicity of the photon is coupled to the valley spin polarization of electrons. Thus, circularly polarized optical excitation into a TMD/graphene heterostructure generates spin polarization in the TMD that subsequently transfers to the graphene. This optical spin injection into graphene is an example of new functionality for the expanding field of 2D spintronics. In the area of 2D magnets, we have used molecular beam epitaxy (MBE) to deposit monolayer $MnSe_2$, which exhibits ferromagnetism at room temperature [2]. These results open the door for new possibilities for magnetoelectronic applications with low dimensional materials.

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4:00pm **2D+EM+MN+NS-ThA6 Giant Electromechanical Response in Van-der-Waals Layered Crystals**, ***Sabine Neumayer***, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; E.A. Eliseev,* National Academy of Sciences of Ukraine*; A. Tselev,* CICECO and Department of Physics, University of Aveiro, Portugal*; A.N. Morozovska,* National Academy of Sciences of Ukraine*; M.A. Susner, M.A. McGuire,* Oak Ridge National Laboratory*; J. Brehm, S. Pantelides,* Vanderbilt University*; N. Balke, P. Maksymovych,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Obtaining ultrathin electromechanically active materials for memory and energy applications encounters numerous challenges as significant downscaling of classical ferroelectrics such as perovskite oxides is severely constrained by size and screening effects. Moreover, interfacing pseudo-cubic ferroelectrics with 2D electronic materials faces challenges related to defect and impurities, which limit performance. Van der Waals ferroelectrics, especially transition metal thiophosphates such as copper indium thiophosphate (CIPS) yield promising prospects for applications as ultrathin piezoelectric structures and interface materials due to their stable surfaces, layered structure and transition temperatures near room temperature. Here, we use scanning probe microscopy to explore the remarkable functional properties of CIPS across the transition temperature. At low temperatures, strong electromechanical response is measured despite the small polarization values and the material contracts in electric fields rather than expanding. These findings point to giant negative electrostrictive coefficients, which were quantified using Landau-Ginzburg-Devonshire analysis. Above the transition temperature, CIPS shows dielectric tunability comparable to BST at low frequencies. In addition, electromechanical strain exceeding 10 nm displacement was measured upon fully reversible field induced formation of particles on the surface. Complimentary DFT calculations provide further insight into the role of ionic displacement in electromechanical behavior.

Research conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility . Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy.

4:20pm **2D+EM+MN+NS-ThA7 A Universal Method for Measuring Valleytronic Quality of 2D Materials using Conventional Raman Spectroscopy**, ***Steven Vitale***, *J.O. Varghese, D.A. Nezich, M. Rothschild,* MIT Lincoln Laboratory

Valleytronics offers a new information processing paradigm based on the momentum index of real or quasi-particles in 2D materials as the fundamental unit of information storage instead of charge. A major challenge to realize valleytronic computing is the development of deterministic material growth processes which yield valleytronic-quality material with the requisite valley relaxation lifetime (T1) and valley dephasing time (T2). Unfortunately direct measurement of T1 and T2 requires complex instrumentation to perform ultrafast spectroscopic measurements and thus is not practical for routine material analysis. In this paper, we demonstrate that an accurate and reproducible measurement of $T1/T_{exc}$ (where T_{exc} is the exciton recombination lifetime) can be performed a simple Raman microscope. By simultaneously measuring the photoluminescence of the 2D material and the Raman transition of the underlying silicon substrate as a function of the incident laser polarization angle, one can remove sources of error and equipment-to-equipment variability. This technique is completely general and can be applied to any valleytronic material which can be grown-on or transferred-to a Raman-active crystalline substrate, such as silicon. Using this technique we show that valley relaxation in a sample of CVD-grown MoS_2 is an order of magnitude slower at 4 K than at 100 K. Oxidation of MoS_2 left exposed to the ambient environment severely decreases the valleytronic quality of the material. Two-dimensional mapping of the valley relaxation time of CVD MoS_2 domains at 4 K shows a three-fold spatial symmetry which is suggestive of new valley physics phenomena which arise in 2D crystals of finite size. MoS_2 domain size also affects the valley relaxation time, which has significant material-growth implications for real valleytronic applications. Finally we compare these measurements to our calculated requirements for valley relaxation time in a practical information processing device and quantify the challenges for future valleytronic material growth.

4:40pm **2D+EM+MN+NS-ThA8 Discovery of Intrinsic Ferromagnetism in 2D van der Waals Crystals***, **Xiang Zhang**, C. Gong,* University of California, Berkeley **INVITED**

In this talk, I will present our discovery of the intrinsic ferromagnetism in 2D van der Waals (vdW) crystals, including the prominent dimensionality effect and unprecedented magnetic field control of the Curie temperature in the nearly-ideal 2D Heisenberg ferromagnet. Significant fundamental physics in 2D magnetism and the corresponding exotic phenomena we observed will be expounded. Updated research on the complex magnon scatterings, material level engineering of 2D magnetism, and the development of novel concept of spintronic devices will be further discussed. Finally, I will envision the possible directions towards advancing 2D magnets for practical spintronic applications.

5:20pm **2D+EM+MN+NS-ThA10 Spectroscopic Evidence of Pair-mediated Bosonic Modes in Superconductor FeSe/SrTiO₃(100) Film***, **Minjun Lee**,* Seoul National University, Republic of Korea*; M. Oh, H. Jeon, S. Yi, I. Zoh,* Seoul National University, Republic of Korea*; C. Zhang,* Seoul National University, Republic of Korea*; J. Chae, Y. Kuk,* Center for Quantum Nanoscience, Institute for Basic Science, Republic of Korea

Single layer FeSe on $SrTiO_3(100)$ is atypical but noticed system in superconductivity. This has unique properties due to the substrate phonon. Unlike other bulk systems, the presence of the interface allows the substrate phonons to affect the superconducting layer. We have investigated substrate phonon effects on superconducting FeSe layer by using scanning tunneling spectroscopy and Eliashberg theory. We were able to measure acoustic, optical and substrate phonons in d^2I/dV^2 spectroscopy. We found these phonon modes attribute to the paring of electrons in this superconducting layer. These results are analyzed by Eliashberg model and we will discuss the coupling strength of these bosonic features. We have found that the substrate phonon has major contribution to increase the transition temperature of this system.

Actinides and Rare Earths Focus Topic
Room 202C - Session AC-ThA

Early Career Scientists

Moderators: Tomasz Durakiewicz, National Science Foundation, David Shuh, Lawrence Berkeley National Laboratory

2:20pm **AC-ThA1 Complexation, Characterization and Separation of the Lanthanides and Actinides: Shedding Light to Subtle Differences within the f-element Series***, **Gauthier Deblonde**, C.H. Booth,* Lawrence Berkeley National Laboratory*; M. Kelley, J. Su, E. Batista, P. Yang,* Los Alamos National Laboratory*; A. Müller, P. Ercius, A.M. Minor, R.J. Abergel,* Lawrence Berkeley National Laboratory **INVITED**

From the nuclear fuel cycles to the therapeutic use of radioisotopes for cancer diagnostics and treatment, the solution chemistry of lanthanides and actinides has become increasingly relevant to a number of applied problems. Understanding the fundamental bonding interactions of selective metal assemblies and the intrinsic differences between f-elements presents a rich set of scientific challenges and is critical to the development of highly efficient separation reagents and new actinide- or lanthanide-based therapeutics.

Our approach to these challenges uses a combination of techniques (EXAFS, liquid-liquid extraction, protein crystallization, UV-vis, fluorescence, DFT…) to characterize f-block aqueous complexes with highly selective and bio-inspired chelators or with more classical aminocarboxylate ligands. With the goal of always minimizing the amount of radioactive material needed and the worker's radiation exposure, we are also investigating the use of TEM spectroscopy to characterize inorganic salts of heavy actinides ($BkCl_3$, $CfCl_3$...) while using only a few nanograms of actinides.

Our journey into the chemistry of the f-elements, and especially that of Am, Cm, Bk, and Cf, led us to capture subtle difference within the trivalent actinide series. A broad study on the aminocarboxylate complexes of Am^{3+}, Cm^{3+}, Bk^{3+}, and Cf^{3+} by EXAFS spectroscopy revealed an unexpected change in speciation between the Cf chelates and its Am, Cm, and Bk analogues. Similarly, the study of the chelation of the lanthanide and actinide cations by some bio-inspired chelators (ex: siderophore derivatives), led us to develop versatile and highly efficient liquid-liquid extraction processes for the purification radioisotopes.

3:00pm **AC-ThA3 Improving the Understanding of Actinides Through Spectroscopy***, **Samantha Cary**, J. Su,* Los Alamos National Laboratory*; S.S. Galley, T.E. Albrecht-Schmitt,* Florida State University*; E. Batista, M.G. Ferrier, S.A. Kozimor, V. Mocko, B.L. Scott, B.W. Stein,* Los Alamos National Laboratory*; F.D. White,* Florida State University*; P. Yang,* Los Alamos National Laboratory **INVITED**

Understanding the fundamental aspects of bonding is important in predicting an element's behavior, unfortunately when it comes to the actinides, there is little known. Acquiring a better understanding of these elements will affect a number of different areas including nuclear forensics, national security, and nuclear fuel cycles. Here we will describe the preparation of $M(S_2CNEt_2)_3(X)$ (M^{III} = Nd, Sm, Eu, Gd, Am, Cm, and Cf; X = *n*-heterocyclic aromatic ligands) and compare their structure, X-ray absorption spectroscopy, and electronic structure calculations.

4:00pm **AC-ThA6 Structural Chemistry of M(IV) (M = Ce, Th, and U) Complexes Isolated from Aqueous Solution***, **Karah Knope**,* Georgetown University **INVITED**

Understanding actinide metal ion speciation and reactivity is of great strategic and scientific importance, and relates to a number of areas ranging from waste management to separations chemistries. Speciation depends on oxidation state, and our knowledge of the structural and energetic properties of tetravalent actinide complexes is relatively limited in comparison to the higher valent oxidation states. This lack of structural and chemical information has resulted in large discrepancies in thermodynamic data, significant challenges in process chemistry, and unanticipated behaviors in environmental systems. As a means of filling this knowledge gap, we have been examining the solid-state structural chemistry of tetravalent Ce, Th, and U complexes obtained from aqueous solutions with an eye towards understanding the directing effects of inner and outer coordination sphere interactions. Moreover, using spectroscopic and X-ray scattering techniques, we have been probing the correlation between the precipitated phases and the solution phase species. Presented here will be an overview of recent efforts to elucidate the effects of both inner- and outer- coordination sphere interactions on the structural chemistry of tetravalent metal ion (Ce, Th, and U) complexes. How the synthetic conditions, identity of the counter-ions, and nature of complexing ligands affect the speciation and reactivity of the Ce(IV), Th(IV)- and U(IV)-building units will be discussed.

4:40pm **AC-ThA8 Hundess, Coherence and Magnetism in URu2Si2- and USb2-family Materials***, **L. Andrew Wray**, L. Miao, H. He,* New York University*; S. Ran,* University of Maryland, College Park*; N.P. Butch,* Nist / Umd*; J.D. Denlinger, Y.-D. Chuang,* Advanced Light Source, Lawrence Berkeley National Laboratory **INVITED**

The uranium compounds URu_2Si_2 and USb_2 present fascinating low temperature phase diagrams, and are focal points of long-standing debates regarding how the crossover between strong correlations and electronic itinerancy should be conceptualized and evaluated. It has recently been found that uranium O-edge resonant X-ray spectroscopies can help to image this multi-natured wavefunction by providing a fingerprint of the f-electron atomic multiplet states. I will present a systematic O-edge spectroscopic characterization of URu_2Si_2 and USb_2 as a function of doping, and show that these data align well with a “Hund's metal” picture for both compounds. Distinct differences in the degree of “Hundess” (same-atom alignment of electron magnetic moments) as a function of chemical composition are found to underlie important features of the low temperature phase diagrams, such as the transition from a “hidden order” phase to antiferromagnetism, and the loss of a low temperature coherence feature in transport measurements. Based on these results, I will propose that developing a more quantitative experimental characterization of Hundness in many-body wavefunctions is of fundamental importance to the broader goal of understanding the phase diagrams in metallic systems with non-trivial local moment physics.

Applied Surface Science Division
Room 204 - Session AS+NS-ThA

Profiling, Imaging and Other Multidimensional Pursuits

Moderators: Ashley Ellsworth, Physical Electronics, Jordan Lerach, ImaBiotech Corp.

2:20pm **AS+NS-ThA1 Surface Science Study of Au/Ni/Cr/n-SiC and Au/Cr/Ni/n-SiC Thin Film Ohmic Contact Material***, **Martyn Kibel**,* La Trobe University, Australia*; A.J. Barlow,* La Trobe University, Australia*; P.W. Leech,* RMIT University, Australia

Silicon carbide (SiC) has become a promising semiconductor material for use in elevated temperature and high power devices. Although ohmic contacts to n-SiC have been widely fabricated using a metallization of Ni/n-SiC annealed at ~1000 °C, the formation of nickel silicides at the interface has resulted in uneven roughening of the metal surface. We have examined for the first time the development of ohmic contact materials containing layers of both Ni and Cr (Au/Ni/Cr/n-SiC and Au/Cr/Ni/n-SiC). A detailed study of these layered structures, both as-deposited and subsequently annealed at 750-1000°C has been undertaken using a range of surface analysis techniques. Auger electron spectroscopy (AES) depth profiling, both static and using Zalar rotation, has been used to etch through the layers into the epitaxial SiC. AES elemental mapping, in conjunction with SEM imaging, has been used to record the nature of the surface before and after profiling. AES line scans have also been employed to characterize the subsequent crater walls. In addition, X - ray photoelectron spectroscopy (XPS) depth profiling has been used to characterise the interfaces with a focus on the chemical states of the constituent elements. The nature of the interfaces between individual layers is discussed as well as the methodologies for generating depth profiles from the acquired data. The analysis has shown a wide-scale interdiffusion of the layers after annealing of the Au/Ni/Cr/n-SiC structure with the formation of surface globules. In comparison, the Au/Cr/Ni/n-SiC contacts have shown a limited interdiffusion of the layers and relatively smooth surfaces, indicating that the intermediate layer of Cr has acted as a diffusion barrier for the Ni. The electrical characteristics of the as-deposited and annealed contacts have been measured using circular transmission line test patterns and the results correlated with the AES and XPS analyses.

2:40pm **AS+NS-ThA2 3D Imaging of InGaN/GaN based Nanowires and Nanotubes using Time-of-flight Secondary Ion Mass Spectrometry***, **Jean-Paul Barnes**,* Univ. Grenoble Alpes, CEA, LETI, France*; A. Kapoor,* Univ. Grenoble Alpes, CEA, France*; C. Durand,* Univ. Grenoble Alpes, CEA, France*; C. Bougerol,* Univ. Grenoble Alpes, CNRS, France*; J. Eymery,* Univ. Grenoble Alpes, CEA, France

GaN based nanowire light-emitting diodes (LEDs) can be grown in ordered arrays on sapphire and large Si substrates. The growth of coaxial InGaN/GaN multiple quantum wells (MQWs) on the nonpolar m-plane sidewalls of the GaN wire increases the active region area, reduces the defect density and can increase efficiency in the case of thick QWs due to the absence of quantum confined Stark effect [1]. Variants on this approach include InAlN/GaN MQW tubes and the integration of such wires in flexible substrates [2].

An important parameter controlling the light emission is the indium concentration in the MQWs and their thickness, which may vary along the length of the wire. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been used to perform 3D mapping of the indium concentration in the coaxial MQWs for both GaN wire geometries and InAlN/GaN MQW tube geometries.

Experiments are performed using a dual beam approach with a finely focused (<200 nm spot size) Bi_3^{++} analysis beam at 60 keV and oxygen sputtering at 500 eV. The indium concentration is calibrated from a 2-D MQW structure on which the nanowires are deposited for analysis so that TOF-SIMS analysis can be performed on the sidewall perpendicular to the MQWs. The TOF-SIMS analysis on single nanowires has allowed the composition of InGaN quantum wells to be quantified and the fact that the MQW structure becomes thicker towards the end of the nanowire to be determined. The ability to target specific nanowires allows the composition determined by TOF-SIMS to be compared with photoluminescence and cathodoluminescence measurements to link the emission of the wires to the MQW composition and thickness. Using a similar approach it was possible to characterize the InAlN/GaN MQWs on nanotube structures and confirm that the MQW structure remains after selective etching of the GaN core and annealing. Such high resolution TOF-SIMS 3D imaging can also be used for other semiconductor structures such as those grown by selective epitaxial growth of for visualising doping in microelectromechanical systems (MEMS) systems.

This work was carried out on the nanocharacterisation platform (PFNC) of the CEA Grenoble.

References:

R. Koester et al. "M-plane core-shell InGaN/GaN multiple-quantum-wells on GaN wires for electroluminescent devices," Nano Letters **11** (11), 4839-4845 (2011).

[2] C. Durand et al. "Thin-Wall GaN/InAlN Multiple Quantum Well Tubes," Nano Letters **17** (6), 3347-3355 (2017).

3:00pm **AS+NS-ThA3 Atom Probe Tomography: Applications and Prospects for Surface and Interface Science***, **Austin Akey**, D.C.. Bell,* Harvard University **INVITED**

Atom Probe Tomography (APT) is a three-dimensional, individual-atom composition mapping technique. Specimens are disintegrated atom-by-atom using a combination of high electric fields and voltage or laser pulses, causing individual ions to be ejected towards a position-sensitive detector with high time resolution. The resulting hit position, combined with the ion's time of flight, allows single-Angstrom, single-atom time-of-flight mass spectroscopy to be performed over volumes containing hundreds of millions to billions of atoms. Recent advances in instrument design and automation have greatly expanded the field of materials systems and scientific questions that the technique can address, and it is particularly well suited to analysis of surface and interface composition.

Datasets can be processed and analyzed as highly-localized 1D composition measurements, 2D surface mapping over an arbitrary surface in three-dimensions, or full volumetric composition maps, allowing a wide variety of questions to be asked of a material. We present applications including: bulk composition fluctuation and clustering measurements; full 3D composition mapping of electronic devices; interface composition and roughness determination; composition mapping of nanowire and other quasi-one-dimensional structures; and surface and bulk composition of catalytic materials. We also discuss the importance of correlating other microanalysis techniques with APT and give examples of one-to-one correlative work. The development of correlative electron microscopy and APT specimen geometries have allowed otherwise unresolvable questions to be answered, and new work extends this into the realm of combined in-situ and ex-situ measurement of the structural and compositional evolution of materials. Finally, we will discuss future prospects for the technique and its application to surface science.

4:20pm **AS+NS-ThA7 Industrial Applications of Surface Analysis in Chemical Mechanical Planarization***, **Hong Piao**, Y.N. Liang, J. McDonough, C. Ballesteros,* FUJIFILM Planar Solutions, LLC, FUJIFILM Electronic materials USA., Inc.*; E. Turner,* FUJIFILM Planar Solutions, LLC, FUJIFILM Electronic materials USA., Inc*; A. Mishra, R. Wen,* FUJIFILM Planar Solutions, LLC, FUJIFILM Electronic materials USA., Inc.

Chemical mechanical planarization/polishing (CMP) is a chemical reaction assisted mechanical polishing process in the semiconductor manufacturing industry to remove overburden material or specific layers in the film stacking and to planarize the topography at the patterned wafer surface. Although the basic principles of CMP are understood, thorough understanding of surface chemical processes which occur during polishing is still lacking, especially the chemistry at the interface of the wafer/slurry/pad. Investigations aimed at understanding fundamental mechanisms usually employ electrochemical techniques. Surface analysis methods remain rather under-utilized in this field, especially when taking into account the explosive growth of these surface techniques for the analysis of "nano-structured" films in other research fields.

FUJIFILM Planar Solutions (PLNR) is a market leader for metals and dielectric CMP slurries. Our in-house XPS and ToF-SIMS surface analysis tools have greatly enhanced our capabilities in analyzing and understanding surface reactions, their mechanism, and fundamental science and engineering behind the slurry wafer interaction at the interface during CMP.

The goal of this presentation is to review selected results provided by advanced surface analysis tools combined with other complementary testing methods. Examples describing CMP characterization are given in two technological areas that are growing in importance: (1) Cu and Co CMP and (2) Defectivity in front end of line polishing involving dielectrics. We also pay particular attention to show how the recent improvements in instrumentation could open new opportunities and fundamental understanding of how surface analyses can enable improvements in slurry design for CMP, thus leading to the development of next-generation advanced CMP slurries and processes.

4:40pm **AS+NS-ThA8 Correlative Images of Microscopy Spectroscopy: Beyond the 3D Characterization in Surface Analysis*, Tanguy Terlier,*** Korea Institute of Science and Technology, Republic of Korea*; R. Verduzco,* Shared Equipment Authority, Rice University*; Y. Lee,* Korea Institute of Science and Technology, Republic of Korea

Technological progress has spurred the development of increasingly sophisticated analytical devices. The full characterization of structures in terms of sample volume and composition is now highly complex. Traditionally, the surface spectroscopic techniques such as AES or ToF-SIMS provide the chemical distribution of sample surfaces. Nevertheless, an important issue in surface analysis is to perform 3D chemical mapping of structured samples with a complex architecture, conserving as well high spatial resolution (lateral and in-depth) as high mass resolution. During the surface analysis, only a projection into 2D surface mapping is achieved which reverse the topographic render after the in-depth analysis. Moreover, the use of ion beam sputtering induces preferential sputtering and damage accumulation due to the sputter beam. So, the surface roughness generated by the sputtering affects the depth profiling of chemical signals. In consequence, the authentic 3D chemical distribution as a function of the depth is completely distorted or lost.

Alternative approaches to resolve the artifacts of 3D chemical images exist. Among these solutions, the use of Scanning Probe Microscopy (SPM) in combination with a surface spectroscopic analysis permits to correct the depth scale of the data and to reduce the artifacts due to the depth profiling. In addition to the data correction, correlative approach using SPM and surface spectroscopy offers the unique possibility to couple topography with 3D chemical information for having access to the accurate volume render. Merging other measurable signals such as electrostatic force microscopy with 3D chemical analysis can also enhanced the understanding of the surface properties and structure characteristics.

After a brief introduction to the data fusion, different methods of 3D reconstruction used in surface analysis will be discussed. In particular, we will show a recent method, the dynamic-model-based volume correction. This method has been applied on a patterned sample using two combination of techniques, SPM/ToF-SIMS and SPM/AES. Then, we have compared the performances of *ex situ* SPM/ToF-SIMS with a new instrument, an *in situ* SPM/ToF-SIMS. To illustrate the new potentials of the correlative imaging method, we have characterized two different samples, a cryo-freezing prepared cell sample and a self-assembled block copolymer film. Finally, we will explore the applications of the correlative microscopy and spectroscopy analyzing a standard SRAM sample that is composed of patterned structures integrating concentration-controlled doping. This sample has provided multi-signal mappings and a quantitative analysis.

5:00pm **AS+NS-ThA9 3D Structure of Atomically Dispersed Metal Species on an Oxide Single Crystal Surface Studied by Polarization-dependent Total Reflection Fluorescence (PTRF)-XAFS*, Satoru Takakusagi,*** *K. Asakukra,* Hokkaido University, Japan

Precise size control of metal species on an oxide surface, especially in the range of <1 nm, is now highly important to develop the next-generation catalysts, sensors, and electronic devices. However this is not easy since metal atoms are easily aggregated to form large particles on an oxide surface. This is due to the small stabilization energy and/or the small activation energy for the metal diffusion. If one can obtain a monatomic metal species on an oxide surface, it can be a building block for synthesis of the metal cluster and helps us to control the cluster size in one-atom precision. Our group has developed the “premodified surface method” to obtain a highly dispersed metal species on an oxide single crystal surface. In the premodified surface method, the oxide surface is precovered with a functional organic molecule possessing a substituent atom which can strongly coordinate to a metal atom before metal deposition. We have determined the precise 3D structures of such metal species by polarization-dependent total reflection fluorescence (PTRF)-XAFS technique.

In this study, various metals such as Cu, Au, Ni and Pt were vacuum-deposited on a $TiO_2(110)$ surface premodified with *o*-mercaptobenzoic acid (*o*-MBA) and their 3D structures were determined by the PTRF-XAFS technique. We have found that Cu, Au and Ni were atomically dispersed by bond formation with sulfur of *o*-MBA and oxygen in the TiO_2 lattice, but Pt was aggregated to form clusters. We will discuss the factors that govern single metal dispersion based on the energy difference between sulfur−metal−oxygen and metal−metal bond formations.

5:20pm **AS+NS-ThA10 XPS Imaging and Spectromiscroscopy Investigation of Extended Release Pharmaceutical Tablets*, Jonathan Counsell,*** *S.J. Coultas, C.J. Blomfield,* Kratos Analytical Ltd, UK*; D.J. Scurr,* The University of Nottingham, UK*; L. Mason,* University of Nottingham, UK*; V. Ciarnelli, J.M. Garfitt, S. Rigby-Singleton,* Juniper Pharma Services Ltd, UK*; M.R. Alexander,* The University of Nottingham, UK*; M.C. Davies,* University of Nottingham, UK*; C. Moffitt,* Kratos Analytical Inc.*; S.J. Hutton,* Kratos Analytical Ltd, UK

The effects of formulation methodology on the performance of tablets have been studied for decades. Typically tablets consist of the active drug and excipients which influence stability, release rate and binding. HPMC (Hydroxypropyl Methylcellulose) is a hydrophilic polymer commonly used in extended-release tablets as it shows rapid hydration and uniform gel formation. The microstructure of HPMC particles in matrices influences the ability of HPMC to form gel layers after contact with water, thereby affecting release characteristics. While previous studies described the use of Raman spectroscopy as a benchmark method for chemically imaging solid pharmaceutical formulations[1], there are relatively few contributions reporting the application of XPS (X-ray Photoelectron Spectroscopy) in this field. New insight into tablet component distribution could be employed in the successful formulation design and development process.

Herein we investigate the novel application of XPS to elucidate the distribution of both drug and excipients species. Parallel XP imaging capabilities will be illustrated and demonstrated for several tablet systems yielding information on particle size, distribution and shape. The use of small-spot XPS provides quantitative and chemical-state information on imaging features. The novel use of argon cluster ion bombardment will be discussed for both cleaning and depth profiling. Peak-fitting, pitfalls and limitations will be explored and compared with other complementary techniques such as ToF-SIMS.

Strachan *et al*. Journal of Pharmacy and Pharmacology. 2007. 179-192.

5:40pm **AS+NS-ThA11 An experimental Guide to Conversion of Tof-SIMS Spectrum to BIG DATA: Application in Analysis of Ultrathin Coatings*, Kevin Abbasi,*** *A.A. Avishai,* Swagelok Center for Surface Analysis of Materials, Case school of Engineering, Case Western Reserve University

Thin films are traditionally being characterized using cross sectional analysis with scanning or transmission electron microscopes. Although accuracy of these technique are very high, it’s hard to analyze a large number of samples this way. Surface analysis instruments such as X-ray photoelectron spectroscopy (XPS), Auger Electron Spectroscopy (AES) and Time-of-flight secondary ion mass spectrometry (Tof-SIMS) can be used to analyze the top surface and erode it with focused ions. Alternating the analysis and ion etching cycles, concentration profiles can be achieved.

In specific conditions where the element of interest has very low concentration or the thickness of the coating is less than the analysis volume (ultrathin films), Tof-SIMS becomes a very powerful tool as it provides the best detection limit and smallest analysis depth. Extracting useful and specific information from the mass spectra and reducing the dimensionality of very large datasets, is a challenge, that has not been fully resolved. Multivariate analysis has been widely deployed to assist in the interpretation of the Tof-SIMS data. Principal component analysis is a popular approach that can help ease the task of analyzing spectrums acquired at different locations from the top surface, compare it against different samples and help extract trends.

The purpose of this talk is to provide experimental guide for the characterization of ultrathin coatings (both flat and in form of particles). Two set of samples will be described: Inter-diffusion will be characterized in a flat coating obtained from Atomic layer deposition (ALD) process and contamination analysis will be then discussed on micron size particles with ultrathin coating. Different strategies will be then discussed to obtain concentration profiles using Time-of-flight secondary ion mass spectrometry. Principal component analysis will then be used to successfully convert mass spectrums into big data and extracting similarities between spectrums and samples.

Biomaterial Interfaces Division
Room 101B - Session BI-ThA

Biolubrication and Wear / Women in Bio-surface Science

Moderators: Anna Belu, Medtronic, Sally McArthur, Swinburne University of Technology and CSIRO

2:20pm **BI-ThA1 Super Lubrication and Extremewear Protection using Bioinspired Polymers***, **Xavier Banquy**, J. Faivre,* Universite de Montreal, Canada*; G. Xie, M. Olszewski,* Carnegie Mellon University*; L. David, T. Delair, G. Sudre, A. Montembault,* Univ. Claude Bernard Lyon I*; K. Matyjaszewski,* Carnegie Mellon University*; R. Shrestha,* Universite de Montreal, Canada **INVITED**

The coming end of earth's fossil energy is pressing humanity to develop more efficient and environmentally friendly technologies. Control of wear and fatigue of machine parts has become one of the most important field of research to meet the outstanding energy crisis the world is currently facing. The design of lubricating fluids able to protect surfaces against wear and high friction has been one the several tools used by engineers to improve machines' life time and decrease energy consumption. Inspired by many different biological systems that can resist fatigue wear for decades such as our synovial joints, different coating/lubricating technologies involving polymer brushes either in their molecular form or grafted on the surface have emerged. All these strategies require the lubricating or wear protecting molecules to be strongly anchored to the surfaces in order to avoid close contact between the surfaces. Strong anchoring of molecules on surfaces requires a good knowledge of the chemistry and the structure of the surface which complicates dramatically the translation of these technologies towards industrial settings.

We will describe our efforts in the design of lubricating and wear protecting fluids based on synergistic mixtures of bottle brushes (BB) and linear polymer solutions that mimic human synovial fluid. Individually, these two polymers exhibit poor wear protecting capabilities compared to saline solutions. Mixture of the two polymers in pure water or in saline allows to drastically increase wear protection of surfaces under a wide range of shearing conditions. We demonstrate that this synergy between the BB and linear polymer emerges from a strong, yet transient, cohesion between the two components forming the boundary film due to entanglements between both polymers. We show that this concept can be applied to other types of linear polymers and surfaces and is independent of the chemical and mechanical properties of the surfaces. We further extended this approach by engineering different types of molecular interactions between the BB polymer and the linear partner and showed that wear protection can be finely tuned independently of the lubricating properties of the mixture. Different applications of these materials will be described in the biomedical field.

3:00pm **BI-ThA3 A Billion Force Runs: The AFM/Single-molecule Version of the Pitch Drop Experiment***, **Laila Moreno Ostertag**,* Vienna University of Technology, Austria*; T. Utzig,* Max Planck Institute for Iron Research, Germany*; C. Klinger,* TU Bergakademie Freiberg, Germany*; M. Valtiner,* Vienna University of Technology, Austria

The "fly-fishing" and breaking of single molecular bonds to study their properties has been extensively studied via Atomic Force Microscopy (AFM) and optical tweezers. A good example for this are various ligand-receptor bonds or surface to molecule bonds such as the gold-amine bond, for which a free energy of ~ 37 k_BT has been determined. The experimental setup and design has evolved over the years, and so have the technology and analysis strategies involved. In the last 15 years, using Jarzynski's equality emerged as a powerful theoretical tool for estimating interaction free energies via the analysis of non-equilibrium work distributions from single-molecule pulling experiments with optical tweezers and AFM. [1] However, some of the questions remain the same and others appear as the field becomes broader. For example, what happens when the chemical model used to connect the probe with the interacting surface and head groups is varied? We recently tested the variation of linker lengths and changing pulling speeds [2] and found strong correlations that confirm the predictions of bias in such experiments by Gore *et al*. [3] in 2003. In particular, the longer the length of the polymeric chain, the more work dissipates during the retraction of the tip, and so does in turn the estimated ΔG_0, which leads to an increasing bias between the average values and those calculated using Jarzynski's equality. This is also reflected in the broadening of work distributions when using the same sample size. Longer polymeric chains show no convergence, unless millions or even billions of events were used. With this order of magnitude in mind, we started our very own "pitch drop experiment": an ambitious project which aims to collect an ever-increasing number of single-molecular force runs for a single system, which will allow us to directly and step-by-step further evaluate equations, work-distributions, convergence behavior, and expected biases in single-molecule experiments. This work will continue along the PhD times of many students - first non-converged results will be discussed in detail and compared to systems that are well converged. Part of this mammoth task is the development of an automated single-molecule recognition algorithm that is capable of distinguishing with high reliability very low work single-molecule events from thermal noise. Some of our advances in this direction will be discussed in detail as well.

References:

[1] Jarzynski, C., *JSMTE* **2004,** *2004* (09), P09005.

[2] Moreno Ostertag, L.; Utzig, T.; Klinger, C.; Valtiner, M., *Langmuir* **2018,** *34* (3), 766-772.

[3] Gore, J.; Ritort, F.; Bustamante, C., *PNAS* **2003,** *100* (22), 12564-12569.

3:20pm **BI-ThA4 Ionic Liquid Behaviour in Biologic Environments: Structuring and Lubrication at Aqueous Solid/liquid Interfaces***, H.-W. Cheng,* TU Wien, Germany*; H. Weiss, M. Mezger,* Max Planck Institute for Polymer Research, Germany*; **Markus Valtiner**,* Vienna University of Technology, Austria

Bio and aqueous applications of ionic liquids (IL) such as catalysis in micelles formed in aqueous IL solutions, lubrication or extraction of chemicals from biologic materials rely on surface-active and self-assembly properties of ILs. Here, we discuss qualitative relations of the interfacial and bulk structuring of water-soluble and highly surface-active ILs on chemically controlled surfaces over a wide range of water concentrations using both force probe and X-ray scattering experiments. Our data indicate that IL structuring evolves from surfactant-like surface adsorption at low IL concentrations, to micellar bulk structure adsorption above the critical micelle concentration, to planar bilayer formation in ILs with <1 wt % of water and at high charging of the surface. Interfacial structuring is controlled by mesoscopic bulk structuring at high water concentrations. Surface chemistry and surface charges decisively steer interfacial ordering of ions if the water concentration is low and/or the surface charge is high. We also demonstrate that controlling the interfacial forces by using self-assembled monolayer chemistry allows tuning of interfacial structures. Both the ratio of the head group size to the hydrophobic tail volume as well as the surface charging trigger the bulk structure and offer a tool for predicting interfacial structures. Based on the applied techniques and analyses, a qualitative prediction of molecular layering of ILs in aqueous systems is possible. Potential applications in biomedical applications will be discussed.

4:00pm **BI-ThA6 Synergistic Mechanisms of Selenium and Tellurium based Nano-Alloys Towards Biofilm Inhibition***, **Kelly Nash**, S. Tek, B. Vincent, C. Smith, R. Robledo,* University of Texas at San Antonio **INVITED**

Selenium (Se) and Tellurium (Te) are two elements under-utilized in medicinal treatments that naturally occur in the human body. Selenium is a bioessential element that exists as a micronutrient throughout most biological systems. In mammalian species, selenium is found in the form of selenocycteine, an amino acid found in selenoproteins. Selenoproteins play an important role in cell metabolism and is an active participant in anti-oxidant glutathione peroxidase mechanism which aids in DNA synthesis. Given selenium's crucial role within biological functions, recent efforts have investigated the antimicrobial properties of selenium as a means to reverse, suppress or prevent the development biofilms. Tellurium, belonging to the same family as oxygen, sulphur and selenium, has been far less studied for its bioactivity. In part, this is due to its classification of being a non-essential biological element. However, recent evidence points to the possible existence and role in biological activity, abet to a lesser extent than selenium. Given that Selenium (Se), a bioessential element, and tellurium (Te), its related analog, are under-utilized elements in the medicinal libraries of antimicrobial treatments, recent research on these elements reveals that they may have numerous therapeutic applications beyond antimicrobial effects including for anti-inflammatory, anti-fouling and anti-cancer treatments. The focus of the work has been to develop novel nano-alloys composed of Se and Te by bio-friendly and chemical free synthesis methods and to evaluate their antimicrobial effects in conjunction with complementary studies on their toxicity against normal cells. Using nano-alloy formulations of these elements will form the basis of a new type of nature-inspired microbial prevention. We demonstrate that the Seand Te nano-alloys provide a reduced toxicity to normal cells while providing enhanced therapeutic efficiency of these compounds towards biofilm inhibition including on surfaces. The short-term impact of this work will provide novel approaches to inhibiting biofilm formation. The long-term impact of this work will provide the basis for treatment of some difficult to treat nosocomial infections caused by *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *E. coli* and *Candida albicans*.

4:40pm **BI-ThA8 From Bedside Back to Bench: Combining Human Centered Design with Biointerfacial Research***, P.A. Nguyen, T. Martin, D. Cuylear, L. Mckenney, B. Matheson, A. Yingling, L. Ista,* ***Heather Canavan,*** University of New Mexico

In 1978, the Worth Health Organization's Alma Ata Declaration asserted individuals' "right and duty to participate individually and collectively in the planning and implementation of their health care". The expansion of these policies began in the 1980s and by the 1990s, social movements across the world demanded greater public accountability and the inclusion of regular citizens in the decision-making process. Today, patient-centered healthcare has continued to progress, and in 2009 a new definition was made by the president of the Institute for Healthcare Improvement Donald Berwick "The experience (to the extent the informed, individual patient desires it) of transparency, individualization, recognition, respect, dignity, and choice in all matters, without exception, related to one's person, circumstances, and relationships in health care". These ideas have transformed over time to become "patient-centered design." In patient-centered design, the focus is to redefine how people experience healthcare by focusing on their needs. The focus of the design is on the wants, needs, and skills of the products' end-users, including patients, doctors, nurses, caretakers, and others.

In our laboratory, we apply our expertise in bioactive and stimulus-responsive polymers, cell/surface interactions, and cytotoxicity to create therapies that improve patient outcomes by improving the patient's experience. For example, we have developed a pH-responsive hydrogel to control the release of the medications used to prepare patients for colonoscopy screening. Using standard surface science techniques such as NMR, FTIR, and XPS, the chemical identity, robustness of the hydrogels in varying environments, and uniformity of size of the hydrogels have been assessed. Using standard cytotoxicity assays such as Live/Dead, XTT, and MTS, the biocompatibility of the hydrogels have been established at increasing concentrations from 1-25% out to four days in vitro with appropriate mammalian cell lines. Our model also shows promise in targeted delivery of biotherapeutics and encapsulated bacterial strains within the GI tract of immunocompromised individuals.

5:00pm **BI-ThA9 Liquid-Infused Surfaces Coated on Paper Improve Bacteria Handling Efficiency and Detection***, D. Regan, C. Lilly, A. Weigang, H. Patanwala,* ***Caitlin Howell,*** University of Maine

Issues such as the rise of antibiotic resistance highlight the need for constant innovation in the field of point of care (POC) microbial diagnostics. Current approaches that do not require the use of energy for storage or detection are hindered by low sample concentration and adhesion challenges which arise when handling these often "sticky" organisms. To overcome these limitations, we combine two approaches in complex analyte handling: infused polymers, which provide a universal anti-adhesion surface against microorganisms, and paper-based microfluidics, which present a lightweight, rugged, and low-cost platform for POC diagnostics, to create paper-supported liquid-infused polymer surfaces. The results showed that the liquid-infused system could be created on multiple different types of paper, including commercially-available silicone release paper which is already manufactured at an industrial scale. Folding the paper liquid-infused surfaces produced chambers which could be used to concentrate the organisms into single point via evaporation with >60% efficiency, compared to <20% efficiency for controls without an infused polymer layer. Sample containing bacteria could be moved from point to point without the loss of cells due to surface adhesion. Finally, integrated proof-of-principle tests showed that the use of liquid-infused surfaces to handle bacteria in this way resulted in positive colorimetric indication of *Staphylococcus aureus* significantly faster than control surfaces. These results demonstrate the use of paper-supported liquid-infused surfaces for improved microorganism handling in POC diagnostics.

5:20pm **BI-ThA10 Tailoring Interactions at the Nanoparticle-nucleic Acid Interface using Molecular Modelling***, M. Manning, J.A. Nash,* ***Yaroslava Yingling,*** North Carolina State University

The design of nanoparticles (NPs) that can induce specific structural transitions in nucleic acids (NA) is important for nanotechnology applications including gene delivery and nanoelectronics. NP biocompatibility and efficacy is determined by geometry, charge, and surface chemistry. Advancing NPs to the clinic requires optimization, which is prohibitively expensive, and a mechanistic understanding of NP-NA interactions, which remains unknown. This project will advance tailored NP gene delivery by a multiscale optimization employing all-atom molecular dynamics (MD) simulations and leveraging machine learning algorithms. It is known that in biological systems, the binding of cationic proteins induces structural changes in DNA or RNA, which can affect gene expression or cause the compaction of DNA into chromatin. The anionic backbone of the nucleic acids DNA and RNA allow for non-specific electrostatic interactions with cationic proteins, nanoparticles, or dendrimers. The interaction of nucleic acids and nanoparticles may be tuned through changes in nanoparticle size, charge, polarity, or shape. However, the factors that affect structural transitions are not fully understood. We performed atomistic molecular dynamics simulations of the binding of nucleic acids to monolayer-protected gold nanoparticles to elucidate structural changes that take place for nanoparticles and DNA upon binding. Results from these simulations were analyzed to determine modes of DNA and RNA bending with nanoparticles. Our simulations show that highly charged nanoparticles cause DNA to bend with little damage to the helix structure, similar to DNA in the nucleosome. Nanoparticle shape as well as charge is shown to affect the wrapping of nucleic acids with the nanoparticle. Low salt concentrations and high nanoparticle charge cause greater disruptions to DNA structure. We find that the roll parameter is the most important base-pair parameter for DNA bending. Requirements for bending differed significantly between DNA and dsRNA. The degree of DNA bending is controlled by the charge of the NPs, but ligand flexibility played a more significant role in dsRNA bending. These results allowed us to determine the training data for machine learning algorithms and design a novel ligands capable of controlled wrapping of NA around NP. We have shown that the designer gold NPs are capable of wrapping NAs with fine control of binding strength through NP charge and ligand stiffness. These findings are useful for designing gene delivery systems with enhanced biocompatibility and selectivity.

5:40pm **BI-ThA11 Biomolecule Interaction with Polymer Thin Films Based on Zwitterions and Polymer Nanoparticles***,* ***Eva Bittrich****, C. Naas,* Leibniz-Institut für Polymerforschung Dresden e.V., Germany*; F. Mele,* Leibniz-Institut für Polymerforschung Dresden e.V. and Polytechnic University of Turin, Italy*; A. Münch,* Leibniz-Institut für Polymerforschung Dresden e.V., Germany*; P. Uhlmann,* Leibniz-Institut für Polymerforschung Dresden e.V.,Germany*; D. Appelhans, K.-J. Eichhorn, B. Voit,* Leibniz-Institut für Polymerforschung Dresden e.V., Germany

Controlling and understanding the interaction behavior of biomolecules with polymer surfaces is one key aspect for the design of new biomaterials. Thin hydrogel coatings offer a huge variety of possibilities to tune physical and chemical surface properties and to create functional biocompatible interfaces supported on a substrate material. Among polymer architectures studied for biocompatible systems are dendritically structured polycations decorated with oligosaccharide shell [1, 2], and zwitterionic copolymers based on phosphorylcholine groups [3]. We prepared two types of thin hydrogel films: 1) based on dendritic polymer core-shell nanoparticles of hyperbranched poly (ethylene imine) (PEI) with maltose shell and 2) based on the statistical copolymer poly[(2-methacryloyloxyethyl phosphorylcholine)-co-(glycidyl methacrylate)] (MPC-*co*-GMA). For both surface types swelling and the interaction with selected biomolecules from small drug molecules to proteins and phospholipids was analyzed quantitatively by in-situ spectroscopic ellipsometry and quartz crystal microbalance with dissipation monitoring. The adsorbed amount of biomolecules was correlated to changes in hydration, thickness and viscoelastic properties of the films to obtain new insights into the specific interaction processes.

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Electronic Materials and Photonics Division
Room 101A - Session EM+2D+NS+PS+RM+TF-ThA

IoT Session: Flexible Electronics & Flash Networking Session

Moderators: Shalini Gupta, Northrop Grumman ES, Sang M. Han, University of New Mexico

2:20pm **EM+2D+NS+PS+RM+TF-ThA1 Epitaxial Electrodeposition of Electronic and Photonic Materials onto Wafer-size Single Crystal Gold Foils for Flexible Electronics***, **Jay Switzer,*** Missouri University of Science and Technology **INVITED**

Single-crystal silicon (Si) is the bedrock of semiconductor devices due to the high crystalline perfection that minimizes electron-hole recombination, and the dense SiO$_x$ native oxide that minimizes surface states. There is interest in moving beyond the planar structure of conventional Si-based chips to produce flexible electronic devices such as wearable solar cells, sensors, and flexible displays. Most flexible electronic devices are based on polycrystalline materials that can have compromised performance due to electron-hole recombination at grain boundaries. In order to expand the palette of electronic materials beyond planar Si, there is a need for both an inexpensive substrate material for epitaxial growth, and an inexpensive and scalable processing method to produce epitaxial, grain-boundary-free films of metals, semiconductors, and optical materials. Recently, in our laboratory, we have developed a process for producing wafer-size, flexible, and transparent single-crystal Au foils by an electrochemical processing method.[1] Au is epitaxially electrodeposited onto Si using a very negative applied potential. An interfacial layer of SiO$_x$ is then produced photoelectrochemically by lateral undergrowth. The Au foil is then removed by epitaxial lift-off following an HF etch. We will report on the electrodeposition of epitaxial films of metal oxide semiconductors such as Cu$_2$O and ZnO onto the highly-ordered and flexible Au foils. We will also present new, unpublished results in which we spin-coat epitaxial films of perovskites, such as CsPbBr$_3$, directly onto these Au foils and onto other single crystals.

Acknowledgement: This presentation is based on work supported by the U.S. Department of Energy, Office of Basic Sciences, Division of Materials Science and Engineering under grant No. DE-FG02-08ER46518.

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3:00pm **EM+2D+NS+PS+RM+TF-ThA3 Flexible Electronic Devices Based on Two Dimensional Materials***, R. Kim, N.R. Glavin,* Air Force Research Laboratory*; R.H. Rai, K. Gliebe, M. Beebe,* University of Dayton; Air Force Research Laboratory*; J. Leem, S. Nam,* University of Illinois at Urbana-Champaign*; R. Rao,* Air Force Research Laboratory*; **Christopher Muratore,*** University of Dayton*; K.M. Burzynski,* University of Dayton and Air Force Research Laboratory, Materials and Manufacturing Directorate

Low temperature synthesis of high quality 2D materials directly on flexible substrates remains a fundamental limitation towards realization of robust, strainable electronics possessing the unique physical properties of atomically thin structures. Here, we describe room temperature sputtering of uniform, stoichiometric amorphous MoS$_2$, WSe$_2$, and other transition metal dichalcogenides and subsequent large area (>2 cm^2) photonic crystallization to enable direct fabrication of two-dimensional material photodetectors on large area flexible PDMS substrates. Fundamentals of crystallization kinetics for different monolithic and heterostructured TMDs are examined to evaluate this new synthesis approach for affordable, wearable devices. The photodetectors demonstrate photocurrent magnitudes and response times comparable to those fabricated via CVD and exfoliated materials on rigid substrates and the performance is unaffected by strains exceeding 5%. Other devices and circuits fabricated from crystallized 2D TMDs deposited on large area flexible substrates are demonstrated.

3:20pm **EM+2D+NS+PS+RM+TF-ThA4 Contact Resistances and Schottky Barrier Heights of Metal-SnS Interfaces***, **Jenifer Hajzus**, L.M. Porter,* Carnegie Mellon University*; A. Biacchi, S. Le, C. Richter, A. Hight Walker,* National Institute of Standards and Technology (NIST)

Tin(II) sulfide (SnS) is a natively p-type, layered semiconductor that is of interest for two-dimensional and optoelectronic applications. Understanding the behavior of contacts to SnS is essential for its use in devices. In this work, contact metallizations with a range of work functions were characterized on both solution-synthesized, p-type SnS nanoribbons and electron-beam evaporated, polycrystalline SnS thin films. The structure and properties of electron-beam evaporated SnS films were dependent upon deposition temperature and post-deposition annealing. A deposition temperature of 300 °C followed by vacuum annealing at 300 °C resulted in p-type, orthorhombic SnS films. Specific contact resistances of Ti/Au, Ru/Au, Ni/Au, and Au contacts were measured on SnS films using circular transfer length method (CTLM) patterns prior to and after annealing the contacts at 350 ° C in argon. All metallizations on SnS thin films were ohmic prior to annealing. A trend of decreasing average specific contact resistance with increasing metal work function was observed for the as-deposited contacts. Annealed Ru/Au exhibited the lowest average specific contact resistance of ~1.9 x 10^{-3} Ω -cm^2. Contacts were additionally patterned onto individual, solution-synthesized SnS nanoribbons. In contrast to the behavior of contacts on electron-beam evaporated films, low work function metals (Cr/Au and Ti/Au) formed Schottky contacts on SnS nanoribbons, whereas higher work function metals (Ni/Au and Pd/Au) formed ohmic or semi-ohmic contacts. Ni/Au exhibited a lower contact resistance (~10^{-4} Ω cm^2 or lower) than Pd/Au (~10^{-3} Ω cm^2 or lower). Schottky barrier heights and ideality factors of Cr/Au and Ti/Au contacts were extracted by fitting current-voltage measurements to a back-to-back Schottky diode model. The ohmic behavior for Ni/Au and Pd/Au and the calculated Schottky barrier heights (0.39 and 0.50 eV for Cr/Au and Ti/Au, respectively) on SnS nanoribbons agree well with behavior predicted by Schottky–Mott theory and suggest a lack of Fermi level pinning.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 201A - Session HC+SS-ThA

Bridging Gaps in Heterogeneously Catalyzed Reactions

Moderator: Ryan Brown, Clarkson University

2:20pm **HC+SS-ThA1 Hydrogen Adsorption and Reaction on RuO$_2$(110) Surface***, A. Dahal, I. Lyubinetsky, **Zdenek Dohnalek,*** Pacific Northwest National Laboratory

Ruthenium dioxide is used extensively as a co-catalyst in a wide range of photocatalytic water splitting systems. As such, understanding how it promotes the evolution of hydrogen and oxygen is of high importance. In our studies, we employed scanning tunneling microscopy in combination with moleculear beam scattering and temperature programmed desorption studies to follow adsorption, reaction, and thermal evolution of hydrogen on a model RuO$_2$(110). In our temperature-dependent studies, we find that at low coverages (H_2/Ru < 0.2) H_2 dissociates heterolytically and forms hydride-hydroxyl pairs below 100 K. At higher coverages (H_2/Ru > 0.2), H_2 adsorbed on Ru sites neighboring the hydride-hydroxyl pairs chemisorbs molecularly. Upon annealing the hydride species convert to hydroxyls and most of the chemisorbed H_2 desorbs. Upon heating, the low and high H_2 covered surfaces transform to partially and fully hydroxylated surface, respectively, above 250 K. Molecular beam scattering studies reveal that the adsorption probability of hydrogen on this surface is strongly temperature-dependent, decreasing from ~0.4 at 25 K to <0.01 at 300 K. These combined studies unravel a complete adsorption and dissociation mechanism of H_2 on this model ruthenium dioxide surface.

2:40pm **HC+SS-ThA2 The Role of Oxides for CO Oxidation over Pd and Rh, and How to Deal with Oxygen Poisoning***, **Johan Gustafson,*** Lund University, Sweden*; O. Balmes,* MAX IV Laboratory, Sweden*; C. Zhang,* Lund University, Sweden*; M. Shipilin,* Stockholm University, Sweden*; A. Schaefer,* Chalmers University of Technology, Gothenburg, Sweden*; B. Hagman,* Lund University, Sweden*; L. Merte, N.M. Martin, P-A. Carlsson,* Chalmers University of Technology, Gothenburg, Sweden*; M. Jankowski,* ESRF, France*; E.J. Crumlin,* Advanced Light Source, Lawrence Berkeley National Laboratory*; E. Lundgren,* Lund University, Sweden

Catalytic CO oxidation is a seemingly simple reaction between CO and O_2 molecules, one of the reactions in automotive catalytic converters, and the fruit-fly reaction in model catalysis. Surprisingly, the phase responsible for the catalytic activity is still under debate, despite decades of investigations. We have performed a simple but yet conclusive study of single crystal Rh and Pd model catalysts, resolving this controversy. For Rh, the oxygen covered metallic surface is more active than the oxide, while for Pd, thin oxide films are at least as active as the metallic surface, but a thicker oxide is less active [1]. The difference between these oxide structures is that the thin PdO films expose coordinatively unsaturated (CUS) metal atoms that act as active sites, while Rh oxides and thicker PdO films do not expose such sites and are hence less active. Similar results have also been found for methane oxidation over Pd [2].

Under highly oxidizing conditions, which are, for instance, desirable for optimal efficiency of combustion engines, there is a general problem of deactivation of catalysts due to too high oxygen exposure, so-called oxygen poisoning. With the above results in mind, this problem is likely related to the formation of oxides that do not expose CUS sites. We therefore believe that the problem of oxygen poisoning over Pd catalysts can be solved by growing a PdO film on top of a more inert metal such as Ag or Au, as this will limit the thickness of the oxide film and hence stabilize the active oxide surface.

In this presentation, we will discuss the active phase of Pd and Rh for CO oxidation, and hopefully show the first results of lower degree of oxygen poisoning for CO and methane oxidation over Pd/Au and Pd/Ag systems.

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3:00pm **HC+SS-ThA3 Simplifying the Relationships between Catalyst Structure and Reaction Rates for Complex Mechanisms***, **Charles T. Campbell**,* University of Washington **INVITED**

Better catalysts and electro-catalysts are essential for many energy and environmental technologies of the future. Designing better catalysts requires knowing the relationships between catalyst structure and catalytic reaction rates, which are in general poorly understood. I will review here some concepts that clarify and simplify these relationships. While a typical catalytic reaction has a dozen or more adsorbed intermediates and elementary-step transition states, Degree of Rate Control (DRC) analysis can be applied to a microkinetic model of the best known catalyst material to show that the net rate really only depends upon the energies of a few (2 to 4) of these. For related materials, one only needs to know how the change in material affects the energies of these few ‘rate-controlling species’ to understand how rates relate to structure. This offers opportunities for designing better catalysts. DRC analysis also provides a simple way to predict kinetic isotope effects (KIEs), which can be compared to simple KIE experiments to verify the energy accuracy of a microkinetic model (that is often based on DFT energies). Such DFT energies can be used with DRC values to predict faster catalysts.

The chemical potential of metal atoms (u_m) in supported catalyst nanoparticles provides another simplifying concept for developing structure – rate correlations in catalysis. It has been known for years that this chemical potential enters directly into the rate equations for catalyst deactivation by sintering. I will show here that it also correlates strongly with the strength with which surface metal atoms bind adsorbed reaction intermediates (and transition states), which correlate with rates as outlined above. I will then review what aspects of catalyst structure control metal chemical potential. It can be tuned to lower values (relative to large particles of the pure metal) by mixing the metal with another metal with which it forms an exothermic alloy, and tuned higher by making the nanoparticles smaller and putting them on a support to which they have a smaller adhesion energy (E_{adh}). Quantitative equations that predict how u_m varies with size and E_{adh}, and how E_{adh} depends on the metal element and the oxide surface used as the catalyst support will be presented. These also offer opportunities for predicting faster catalysts.

· Work supported by NSF and DOE-OBES Chemical Sciences Division.

4:00pm **HC+SS-ThA6 Spectroscopic Techniques for Identifying Reactive Intermediate Structures during Decomposition of Formic Acid over Metals and Metal Oxides***, **Megan Witzke**, D.W. Flaherty,* University of Illinois at Urbana-Champaign

Identifying reactive intermediates within an “organometallic zoo” of species that form on surfaces of metal nanoparticles and metal oxides during reactions is a long standing challenge in heterogeneous catalysis.[1] We use a combination of spectroscopic techniques and data analysis methods to isolate and extract spectral features of the reactive intermediates present under relevant operating conditions. Modulation excitation spectroscopy coupled with phase sensitive detection selectively filters spectra to show only reactive intermediates and suppress features of spectating species.[2] The combined spectra of all reactive species are deconvoluted using singular value decomposition techniques that provide distinct spectra and estimate surface coverages for independent species.[3] Comparisons of spectra obtained at different modulation frequencies exploit differences in intrinsic free energy barriers between reactive intermediates by removing species that are unable to form at higher stimulated frequencies. We combine these techniques to molecularly interpret infrared spectra to identify compositionally similar surface intermediates formed in situ during decomposition of formic acid (HCOOH) over anatase TiO_2 and Au-TiO_2. Operando and transient measurements determine the sequence of elementary steps that decompose HCOOH and identify surface species that do not form CO and CO_2. Transient measurements show that HCOOH adsorbs and deprotonates to form bidentate formates over TiO2 while monodentate intermediates do not lead to CO or CO_2 formation. Selective inhibition of Au sites with co-fed CO over Au-TiO_2 indicate monodentate reactive intermediates evolve into bidentate formates on Au at higher coverages. Distinguishing the structure, composition, and orientation of reactive intermediates provides complimentary evidence to measured rates and DFT to depict reaction mechanisms and provide insight into how surface properties dictate rate and selectivity.

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4:20pm **HC+SS-ThA7 Self-sustained Reaction Oscillations in a New Light***, **Uta Hejral**, S. Albertin, J. Zhou, S. Pfaff,* Lund University, Sweden*; M. Shipilin,* Stockholm University, Sweden*; S. Blomberg,* Lund University, Sweden*; O. Gutowski, A. Dippel,* Deutsches Elektronen-Synchrotron DESY, Germany*; J. Gustafson, J. Zetterberg, E. Lundgren,* Lund University, Sweden

Catalysts are complex material systems accelerating desired chemical reactions in chemical industry, fuel cells and car exhaust treatment. To improve their performance, an atomic-scale understanding of the interplay between catalyst structure, the surrounding gas composition and the catalyst activity under realistic reaction conditions is inevitable. Self-sustained reaction oscillations, in which the catalyst shuts its activity periodically off, have been studied for many years [1, 2] with the aim (1) to avoid reactor instabilities or even reactor explosions, and (2) to understand and make use of the underlying catalyst structures leading to higher conversion rates and selectivities often present during the oscillations. However, no general mechanism, especially for the structure leading to the activity increase and decrease, has been put forward.

Here we combined High Energy Surface X-Ray Diffraction (HESXRD) [3, 4], Planar Laser Induced Fluorescence (PLIF) [5], in-situ Mass Spectrometry (MS) and optical LED reflectance [6] at beamline P07 (DESY) at a photon energy of 77 keV to study self-sustained reaction oscillations during CO oxidation over Pd(001). This allowed, with sub-second time resolution, for correlating the catalyst structure (HESXRD) to the sample’s CO_2 production (PLIF, MS) and hence its catalytic activity. The LED light, reflected from the sample surface, provided in addition immediate information on the surface roughness. Our data indicate that the oxidation and reduction of (111)-oriented Pd islands on top of an epitaxial PdO(101) oxide layer, previously reported under reducing conditions close to UHV [7], play a crucial role in the underlying mechanism for the self-sustained reaction oscillations.

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4:40pm **HC+SS-ThA8 Operando Catalysis--A First-Principles Perspective***, **William Schneider**,* University of Notre Dame **INVITED**

First-principles computational methods have had a profound impact on the science of heterogeneous catalysis. One of the challenges in making these models more rigorous, for instance to establish quantitative relationships between experimental observations of rates, rate orders, and models, is to faithfully account for the influence of the catalytic reaction conditions on the state of a catalytic material and on mechanism. “Operando” experiments interrogate catalysts at the conditions at which they are functioning. In the same way, by incorporating finite temperatures and pressures through statistical mechanical and ab initio dynamics models, and by recognizing that a catalytic material may present a heterogeneous array of sites, it is in principle to model a catalyst "operando" from first principles. In this presentation I first discuss our efforts to model finite-temperature adsorption behavior at metal surfaces, including the translational motions that control adsorption free energies and the interactions between adsorbates that can modify surface reaction kinetics. I then discuss our recent work to describe how the rates of surface reactions might be altered by the imposition of an external plasma, showing how changing the "environment" is an alternative and promising way to control catalytic reactivity.

5:20pm **HC+SS-ThA10 Chiral Selectivity in Heterogeneous Catalysis***, R. Chapleski, **Sharani Roy**,* University of Tennessee Knoxville

Developing powerful next-generation technologies for catalysis, energy conversion, and energy storage relies on understanding and controlling molecular transformations at complex interfaces. However, relatively little is known about the fundamental molecular-scale phenomena driving chemical selectivity at functional and complex interfaces. Our work aims to investigate mechanisms of enantioselectivity in heterogeneous catalysis. Specifically, by investigating hydrogenation reactions of both the (R)- and (S)- enantiomers of limonene on the chiral Pt(532) surface, we will provide insight into the adsorbate-surface interactions that lead to enantiomeric excess in the formation of the chiral product, menthene. Here, we report our initial results of this work, which uses computational methods to probe molecular adsorption of limonene followed by catalytic hydrogenation. Our approach utilizing density functional theory combined with the results of recent experimental sum-frequency generation experiments, reveals likely adsorption orientations and reaction pathways of both enantiomers on the Pt(532) surface. A comparison of adsorption and reaction mechanisms across both enantiomers leads to a fundamental description of the atomic-scale interactions that produce enantioselectivity in adsorption and reactions of limonene on a chiral platinum surface. We hope that these results provide qualitative insight into how enantioselectivity is achieved in heterogeneous catalysis at intrinsically chiral metal surfaces.

5:40pm **HC+SS-ThA11 Combining *in situ* Environmental TEM and Multiscale Simulations to Study the Dynamic Processes of Copper Oxidation***, **Meng Li**, M.T. Curnan, W.A. Saidi, J.C. Yang,* University of Pittsburgh

Cu-based materials are widely used in industrial catalysts applications, including methanol synthesis and H_2 production from the water-gas shift reaction. Across these applications, maximizing the Cu surface area improves the catalytic performance. However, side effects such as poor stability and deactivation also occur due to oxide formation at active sites over long-term use. Therefore, developing a fundamental understanding of the nanoscale mechanisms initiating Cu surface oxidation is essential to addressing these issues. The process of surface oxidation can be divided into three stages, namely oxygen chemisorption, oxide nucleation and growth, and bulk oxide growth. Of these three stages, the initial stage – which spans from the oxygen chemisorption to the onset of oxide nucleation – is least understood, as it is inaccessible to traditional surface science and bulk material experimental methods. Despite recent improvements in computational methods, current computational capabilities have yet to simulate O chemisorption directly leading to oxide nucleation, given the resources required to complete such simulations over sufficiently large time and size scales.

In this work, by combining Environmental TEM (ETEM) with multiscale atomistic simulation, the dynamical processes enabling initial stage copper oxidation were explored. Our ETEM (Hitachi H-9500, 300 kV, LaB_6) results show that over surface step defects of various facet orientations, oxide nucleation preferences vary over adjacent facet edges, potentially leading to known differences in observed reconstructions on differently oriented surfaces. Surface reconstructions on Cu(100) and Cu(110) facets were observed, followed by Cu_2O island nucleation and growth in a layer-by-layer manner. Investigation of the dynamical processes leading to oxide nucleation on these reconstructed surfaces is done via a multiscale computational approach. Single initial oxidation stage events from oxygen chemisorption to surface reconstruction are first modeled using the Nudged Elastic Band (NEB) method on systems modeled with Reactive Force Field (RFF) potentials. Oxide nucleation and growth is then affordably modeled at size and time scales consistent with ETEM results, applying structures and energies resolved in RFF NEB calculations to rate tables used by adaptive kinetic Monte Carlo simulations. This simulation methodology forms a feedback loop with ETEM results, allowing computational and experimental results to validate one other. Ultimately, this cross-validation will be used to explain how oxide nucleation can be prevented by controlling factors like surface and defect orientation, temperature and pressure.

Advanced Ion Microscopy Focus Topic
Room 203B - Session HI-ThA

Emerging Ion Sources, Optics, and Applications

Moderators: John A. Notte, Carl Zeiss Microscopy, LLC, Shinichi Ogawa, National Institute of Advanced Industrial Science and Technology (AIST)

2:20pm **HI-ThA1 Development of Gas Field Ionization Source using Gas with Low Ionization Energy that Enables Sample Processing and Observation***, **Shinichi Matsubara**, H. Shichi, T. Hashizume,* Hitachi, Japan **INVITED**

Practical use of a gas field ionization ion source (GFIS) has been tried for decades, but it was known difficult to realize. The GFIS has an extremely high brightness and a small source size, so that the convergence performance is excellent. As the atomic structure formation technology of the emitter tip has matured, the He - GFIS has been used in the real world scanning ion microscopes (SIMs). At first, their application was focused on the observation of the surface of samples because of its surface sensitivity, long focal depth, and a high resolution. Recently, however, Ne - GFIS has also been used for applications on fine direct fabrication which was difficult with a gallium liquid metal ion source.

We are developing GFISs which emit various kinds of ions and their own characteristics has been investigated. We are also developing ion-switching techniques which enable quick switching between fabrications and observations. With these techniques, we expect to create innovative applications difficult to realize with other technologies. In the previous studies we showed that an H_3^+ ion is superior for observation with a low damage. Its energy dispersion is comparable with a He^+ ion (0.5 eV) but the sputtering rate is expected to be smaller. We also showed that the H_3^+ and Ne^+ ions can be switched within 1 s by using a mixed gas of H_2 and Ne, and by changing the emitter voltage. With this technique, we can instantly switch between fabrication and observation. Regarding the Ar-GFIS which is promising for fine fabrication, we showed that the effective fabrication rate given by the product of the current and the sputtering rate is highest among the Ne, Ar and Kr. Furthermore, we have put into practical use of a photomask repairing technology using N_2 - GFIS.

3:00pm **HI-ThA3 Development of Scanning Helium Microscopy (SHeM)***, **Susanne Schulze**, D.J. Ward, M. Bergin, S. Lambrick, W. Allison, J. Ellis, A. Jardine,* University of Cambridge, UK

Some of the major insights in the development of modern materials have come from scanning probe, electron, and ion microscopy, with advances in resolution and sensitivity enabling new material science. While charged particle beam techniques are widely used they have the serious drawback of causing damage to sample surfaces, while scanning probe techniques are limited to relatively flat surfaces and suffer from limited scan speeds. Instead, we are pursuing a different approach, using neutral atom beams. Here we will report on recent advances and development of the scanning helium microscopy (SHeM) technique.

Since SHeM uses a neutral beam of helium atoms at very low energy (<100 meV), the technique is suitable for measuring a variety of samples including insulators, semiconductors, organic and biological species. It is particularly attractive as the approach does not require any complicated post processing techniques. We will report on recent studies on range of materials and potential new applications, including measurements performed in collaboration with colleagues at the University of Newcastle (Australia) [1,2]. A particular focus will be on describing the underlying mechanisms of contrast formation.

Many of the technological challenges associated with SHeM have now been addressed, including helium focusing, sample preparation and nanoscale manipulation, thus enabling preliminary instruments to be developed[1,2,3]. One of the remaining challenges is adequate detection of neutral atom beams, which is a particular problem due to helium's high ionization energy[3]. Applications that require time-sensitive measurements require a small ionization volume; however, when very high temporal resolution is not required, as with SHeM, very large ionizers with high detection efficiencies can be used. We will also report a recently developed detector, based on the approach recently applied to surface spin-echo experiments [4,5,6], and having the highest yet reported sensitivity for helium atoms.

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3:20pm **HI-ThA4 Fabrication of Trimer/Single Atom Tip for GFIS by Field Evaporation without Tip Heating***, **Kwang-Il Kim,*** University of Science and Technology, Republic of Korea*; Y.H. Kim, T. Ogawa,* Korea Research Institute of Standards and Science (KRISS), Republic of Korea*; S.J. Choi,* Kyungpook National University, Republic of Korea*; B. Cho, S.J. Ahn, I.-Y. Park,* Korea Research Institute of Standards and Science (KRISS), Republic of Korea

The application of the helium ion microscope (HIM) has expanded in various fields, such as nano-patterning, material science, and biology, due to its high spatial resolution for imaging and high-precision machining [1-3]. HIM realized sub-nm resolution with gas field ion sources (GFIS) which generate s ion beams from one or three topmost atoms of tips to obtain high beam current density. However, it is difficult to fabricate atomically sharp tips, such as trimer/single atom tip (TSAT), in an ultra-high vacuum (UHV) condition. TSAT can be typically fabricated by either a build-up method or field-assisted reactive gas etching method with oxygen and nitrogen [4-7]. However, these methods usually adopt resistive tip heating at about 1000 K as pre-cleaning of tip surface before the tip sharpening process. This heating leads to complex system because of a power supply circuit to provide or flow a current through a heating loop, where the tip was welded. In our study, we show that TSAT can be fabricated by field evaporation effect with an oxide layer which remains on the tip surface owing to the absence of tip heating.

As the result of this study, we could get a single crystalline field ion microscopy (FIM) image of W(111) with fabricating a TSAT by field evaporation phenomenon without tip surface cleaning by high temperature heating process. The oxide layer which remained after electrochemical etching process induces etch-like phenomenon in UHV condition without any additional gas injection. In order to analyze verify the proposed etching process, the analytical techniques of transmission electron microscope (TEM), energy filtered transmission electron microscope (EFTEM), and electron energy loss spectroscopy (EELS) were used. To compare the etching results whether the insulating layer present or not, we did additional experiment for tip heating. It was found that tungsten oxides contained in the insulating layer of the tip surface causes the etching. This method is much simpler than conventional methods because it uses only field evaporation phenomenon for fabricating TSAT. Therefore, we can simplify the equipment configuration since there is no need to heat the tip.

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4:40pm **HI-ThA8 Avoiding Amorphization Related Shape Changes of Nano-structures during Medium Fluence Ion Beam Irradiation of Semiconductor Materials***, **Xiaomo Xu,** G. Hlawacek, H.-J. Engelmann, K.-H. Heinig,* Helmholtz Zentrum Dresden-Rossendorf, Germany*; W. Möller,* Helmholtz-Zentrum Dresden-Rossendorf, Germany*; A. Gharbi,* CEA-LETI, France*; R. Tiron,* CEA-LETI, MINATEC, France*; L. Bischoff, T. Prüfer, R. Hübner, S. Facsko, J. von Borany,* Helmholtz Zentrum Dresden-Rossendorf, Germany

We present an approach to mitigate the ion beam induced damage inflicted on semiconductor nano-structures during ion beam irradiation. Nanopillars (with diameter a of 35 nm and height of 70 nm) have been irradiated with either a 50 keV Si^+ broad beam from an implanter or a 25 keV focused Ne^+ beam from a helium ion microscope (HIM) . Upon irradiation of the nanopillars at room temperature with a medium fluence (2e16 ions/cm^2), strong plastic deformation has been observed which hinders further device integration. This differs from predictions made by the simulations using TRI3DYN. However, irradiation at elevated temperatures with the same fluence would preserve the shape of the nanopillars.

It is well known that a critical temperature exists for silicon above which it will recrystallize during ion beam irradiation. This prevent s the amorphization of the target material independent of the applied fluence. At high enough temperatures and not for too high flux this prevents the ion beam hammering and viscous flow of the nano-structures. These two effects are responsible for the shape change observed at low temperature. This has been observed previously mainly for swift heavy ions and energies higher than 100 keV. We used HIM and transmission electron microscopy to follow the morphological evolution of the pillars and their crystallinity. While irradiation at room temperature results in amorphization and the related destruction of the nanopillars, irradiation above 650 K preserves the crystalline nature of the pillars and prevents viscous flow. This effect has been observed previously mainly for swift heavy ions and energies higher than 100 keV. Such high-temperature irradiation, when carried out on a nanopillar with Si/SiO2/Si layer stack, would induce ion beam mixing without suffering from the plastic deformation of the nanostructure. Due to a limited mixing volume, single Si-NCs would form in a subsequent rapid thermal annealing process via Oswald ripening and serve as a basic structure of a gate-all-around single electron transistor device.

This work is supported by the European Union’s H-2020 research project ‘IONS4SET’ under Grant Agreement No. 688072.

Magnetic Interfaces and Nanostructures Division
Room 203A - Session MI+BI-ThA

Interdisciplinary Magnetism

Moderator: Markus Donath, Westfälische Wilhelms-Universität Münster, Germany

2:40pm **MI+BI-ThA2 Chiral Induced Spin Selectivity in Molecular Bond Dissociation***, **Richard Rosenberg,*** Argonne National Laboratory

Since nearly all biological compounds are homochiral, any model of the origin of life must be able to incorporate a mechanism that could lead to preferential chirality. Since chiral molecules have a certain handedness, many researchers have investigated the possible influence of circularly polarized UV photons and longitudinal spin-polarized electrons in creating an enantiomeric excess.[1-3] However, in general the demonstrated effects have been small and/or on the order of the experimental error. Previously we demonstrated [4] that chiral-selective chemistry occurs when X-rays irradiate a chiral molecule bound to a magnetic substrate and suggested that a previously unappreciated source may play a role in chiral-selective chemistry: low-energy (0-20 eV) spin-polarized secondary electrons, produced by photon, electron, or ion irradiation. In the present work, we explore a possible alternative mechanism based on the chiral induced spin selectivity (CISS) effect [5] which suggests that the lifetime of an excited electron in a chiral molecule bound to a magnetic substrate should depend on the magnetization direction of the substrate. To investigate this possibility, we examined the photon-stimulated desorption yield of hydrogen ions from D- and L-Hystidine bound to a magnetized cobalt film. The data indicates differences in the N K edge spectra of the H^+ ion yield depending on the substrate magnetization direction. These results suggest a possible CISS effect on the excited state lifetime of the dissociative state. Such a mechanism would be applicable to any process that leads to an excited electron in a dissociative state of a chiral molecule bound to a magnetic substrate. Iron is one of the most common elements and many iron compounds are magnetic, so such a mechanism could be applicable in a wide range of prebiotic environments.

The work performed at the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under contract No. DE-AC02-06CH11357.

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3:00pm **MI+BI-ThA3 The Chiral Induced Spin Selectivity Effect- From Spintronics to Controlling Chemistry**, ***Ron Naaman,*** Weizmann Institute of Science, Israel **INVITED**

Spin based properties, applications, and devices are commonly related to magnetic effects and to magnetic materials. However, we found that chiral organic molecules can act as spin filters for photoelectrons transmission, [i] in electron transfer, [ii] and in electron transport. [iii]

The new effect, termed Chiral Induced Spin Selectivity (CISS), [iv] enables new type of spintronics, [v] has interesting implications in Biology, [vi] varying from allowing long-range electron transfer, controlling multiple electrons reactions, and in enantio-recognition.

The effect and its various applications and implications will be discussed.

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4:00pm **MI+BI-ThA6 Multifunctional Ferromagnetic Disks for Life Sciences Applications**, ***Elena Rozhkova,*** *V. Novosad,* Argonne National Laboratory **INVITED**

The impact of modern nanomaterials and engineered architectures on biological modulation, bioanalytical techniques, and healthcare technologies can hardly be overestimated. Magnetic nanomaterials are attractive for life sciences applications because they can be detected and operated remotely, biological barriers-free, using external magnetic field. Using top-down micro-/nano-fabrication techniques allows for production of monodisperse magnetic particles of virtually any composition and shape, with tunable magnetic properties. Such particles have been exploited as multi-spectral MRI contrast enhancement labels, for *in vitro* detection of molecular markers and cell sorting. This talk will summarize successful applications of lithographically defined disk-shaped particles composed of ferromagnetic $Fe_{20}Ni_{80}$ permalloy core for biomedical applications in both low- and high frequency magnetic field regimes as mediators of biological mechanotrasduction, as delivery vehicles, contrast agents and ultrasensitive detection labels. Advanced synchrotron imaging was used to visualize interaction of engineered nanomagnetic hybrids with living systems and study their chemical stability at subcellular, cellular and 3D multicellular levels.

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4:40pm **MI+BI-ThA8 Magnetic Nanoparticles in Biomedicine: Recent Developments in Imaging, Diagnostics and Therapy**, ***Kannan Krishnan,*** University of Washington **INVITED**

The Néel relaxation of magnetic nanoparticles (MNP), subject to alternating magnetic fields in solution, depends exponentially on their core diameter while the complementary Brownian relaxation mechanism depends critically on their hydrodynamic volume [1]. Recent developments [2] in the synthesis of highly monodisperse and phase-pure magnetite nanoparticles allows for reproducible control of the former in biological environments, enabling novel imaging [3,4] and spectroscopic modalities, under ac excitations such as magnetic particle imaging/spectroscopy (MPI/MPS) with superior resolution and sensitivity [5]. [8] .

Magnetic Particle Imaging (MPI) is an emerging, tracer-based, whole-body medical imaging technology with high image contrast (no tissue background) and sensitivity (~250 nm Fe) to an optimized tracer consisting of an iron-oxide nanoparticle core and a biofunctionalized shell. MPI is linearly quantitative with tracer concentration and has zero tissue depth attenuation. MPI is also safe, uses no ionizing radiation and clinically approved tracers. MPI is also the first biomedical imaging technique that truly depends on nanoscale materials properties; in particular, their response to alternating magnetic fields in a true biological environment needs to be optimized.

In this talk, I will introduce the underlying physics of MPI, the alternative approaches to image reconstruction, and describe recent results in the development of our highly optimized and functionalized nanoparticle tracers for MPI. I will then present state-of-the-art imaging results of preclinical *in vivo* MPI experiments of cardiovascular (blood-pool) imaging [6], stroke [7], GI bleeding [8], and cancer [9] using rodent models. I will also discuss a related diagnostic method using magnetic relaxation and illustrate its use for detecting specific protease cancer markers in solution [10]. If time permits, I will introduce therapeutic applications of magnetic nanoparticles [11].

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MEMS and NEMS Group
Room 202B - Session MN+2D+AN+NS-ThA

Nonlinear and Thermal Resonators

Moderators: Meredith Metzler, University of Pennsylvania, Christian Zorman, Case Western Reserve University

2:20pm **MN+2D+AN+NS-ThA1 Embracing Nonlinearity and Thermal Fluctuations in Nanomechanics**, *D. Lopez,* ***David Czaplewski,*** *C. Chen,* Argonne National Laboratory*; D. Zanette,* Centro Atomico Bariloche, Argentina*; S. Shaw,* Michigan State Univrsity **INVITED**

The field of micro-mechanics is now a well-established engineering domain with demonstrated impact in fundamental science and product development. Unfortunately, as the dimensions of the devices are reduced from the micro- to the nano-scale, the direct scaling of the fundamentals principles and fabrication processes cease to work. When going from micro- to nano-mechanical systems, MEMS to NEMS, the devices linear dynamic range can be reduced to the point where the amplitudes needed for lineal response are below the noise level and, as a consequence, operation in the nonlinear regime is unavoidable. Furthermore, thermal fluctuations and fluctuation-induced forces become relatively stronger causing significant changes in their dynamic response and on the manner in which they interact with the surrounding environment. This combination of nonlinear dynamics and high sensitivity to fluctuations has been seen as a deleterious combination for the advance of nano mechanical devices.

Rather than continuing to struggle to avoid these phenomena, it is of interest to consider how micro/nanosystem might effectively capitalize on this nonlinear fluctuating response. In this talk, I will demonstrate that nonlinearity offers unique possibilities for the controlled response of micro and nano mechanical devices and, thereby, a host of novel application opportunities. Examples of these opportunities include the development of compact frequency sources with low phase noise, the engineering of dissipation reservoirs to manipulate energy decay processes, and the enhancement of synchronization range between microscopic and macroscopic oscillators.

3:00pm **MN+2D+AN+NS-ThA3 Probing Ion Radiation Effects in Silicon Crystals by 3D Integrated Resonating Thin Diaphragms***, **Hailong Chen**, H. Jia, V. Pashaei,* Case Western Reserve University*; W. Liao, C.N. Arutt, M.L. McCurdy,* Vanderbilt University*; P. Hung,* The Aerospace Corporation*; R.A. Reed, R.D. Schrimpf, M.L. Alles,* Vanderbilt University*; P.X.-L. Feng,* Case Western Reserve University

Space radiation (*e.g.*, solar, galaxy) and man-made radiation environments (*e.g.*, nuclear plant) can expose devices to radiation at doses that may lead to severe damage [1]. In recent decades, a large body of work has been performed to understand radiation effects on mainstream solid state electronic devices [1-3], in particular on MOS devices [2] and integrated circuits [3]. Lately, microelectromechanical systems (MEMS) have seen widespread adoption in consumer, military and aerospace products due to their small size, low power consumption, and in some cases, monolithic integration with electronics [4]. As such, the reliability of MEMS devices for many applications in relatively benign environments has been well established [5]. However, the study of impact on mechanical properties due to radiation-induced damages is an area where limited research has been conducted.

In this work, we report on experimental investigation of heavy ion radiation effects on mechanical properties of Si crystals, by exploiting a novel 3D scheme of using 5 vertically stacked micromachined vibrating Si diaphragms (2 mm × 2 mm x 2 µm) exposed to oxygen ions. Simulations find the stop range of oxygen ions in Si is 7.3 µm. A Pelletron system is employed to irradiate oxygen ions into the Si diaphragms (10.3MeV, with a dose of $5.6 \times 10^{13}/\mathrm{cm}^2$). Before and after radiation, multimode resonances are characterized in vacuum by using an ultrasensitive optical interferometry system. We have observed that diaphragms D1 and D2, which oxygen ions are expected to pass completely through, present modest multimode redshifts ranging from 0.85 kHz to 1.67 kHz, and 0.85 kHz to 1.19 kHz, corresponding to an average fractional frequency shift of 10.5% and 7.0%, respectively. In contrast, for devices D3 and D4, in which most ions are expected to stop, each resonance peak shifts much more dramatically, with a frequency shift of 27.3% and 20.4%. We attribute these large shifts to the very large capture area of the diaphragms, the very heavy and energetic oxygen ions, and high ion dose. Device D5 shows minimal frequency shifts among the five diaphragms because few oxygen ions reach and interact with this device layer. The diaphragm stack exhibits outstanding capability for probing radiation damages in MEMS, not only able to capture the radiation events obviously, but also help analyze different amount and types of damages induced in each stacking layer.

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3:20pm **MN+2D+AN+NS-ThA4 An Array of Thermally-actuated Nanoresonators for Real-time Mass Spectrometry***, **Martial Defoort**, M. Sansa, M. Gély, G. Jourdan, S. Hentz,* CEA/LETI-University Grenoble Alpes, France

Micro/Nano-ElectroMechanical Systems (M/NEMS) have attracted much attention in the last years in the mass spectrometry field. They feature high sensitivity, charge independent and single particle detection capabilities, in a mass range where conventional mass spectrometry struggles, hampering the analysis of large mass objects like protein complexes or viruses [1-4].

In general the size and mass of the device defines the size and mass ranges of the particles to measure for frequency tracking and point mass approximation purposes. However, as many silicon M/NEMS are electrostatically actuated, the gap between the driving electrode and the resonator becomes a critical parameter. While for many applications this gap should be as small as possible for high efficiency actuation and high signal-to-noise ratio, a particle landing within the gap results in a catastrophic failure of the device through electrical short-circuit or mechanical anchoring.

We present a new actuation scheme for doubly-clamped beams which rel ies on the thermal expansion of nano-actuators in silicon due to Joule heating, located close to the anchor of the resonator (Fig. 1), that we demonstrate to work in an array of 20 NEMS (Fig. 2). Unlike some thermoelastic actuation schemes [5], the technique we propose does not require an additional layer (of, for example, a metal) and is readily CMOS-compatible. Because of their small size and thermal capacity, the thermal time constant of the actuators is small enough to drive the resonator up to several 100's MHz with large efficiency and to actuate the two first flexural modes of the same device simultaneously, which is required for single particle mass sensing . The detection scheme uses the piezoresistive gauges located on the other end of the beam, as previously presented [6]. We compare the performance of this actuation technique with a standard electrostatic scheme both on the same array and demonstrate the thermal actuation does not affect the level of frequency fluctuations limiting the device mass resolution (Fig. 3).

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2. Sage *et al*, nature communications 2015.
3. Sage *et al*, Arxiv 2017.
4. Dominguez-Medina *et al*, Arxiv 2018.
5. Mo Li *et al*, nature nanotechnology 2007.
6. Mile *et al*, nanotechnology 2010.

4:00pm **MN+2D+AN+NS-ThA6 Nonlinear and Noise Induced Dynamics of High Q Nanomechanical Resonators***, **Jana Huber**, E.M. Weig,* University of Konstanz, Germany **INVITED**

Doubly-clamped pre-stressed silicon nitride string resonators excel as high Q nanomechanical systems enabling room temperature quality factors of several 100,000 in the 10 MHz eigenfrequency range when operated under vacuum conditions. To retain the high mechanical quality factor, dielectric transduction is implemented as an all-electrical control scheme avoiding the metallization of the string. To this end, the string is exposed to an inhomogeneous electric field created between adjacent electrodes. The resulting gradient field provides an ideal platform for actuation, displacement detection, frequency tuning as well as strong mode coupling between the in- and out-of-plane modes of the string.

Here we focus on the nonlinear dynamics of the string subject to a strong drive. As a result of the high quality factor, cubic as well as higher order nonlinearities are observed. In the presence of thermal fluctuations, satellite resonances arise which enable deep insights into fundamental properties of the system.

4:40pm **MN+2D+AN+NS-ThA8 A Buckling-based, DC Controlled, Non-volatile Nanoelectromechanical Logic Memory***, S.O. Erbil, **Utku Hatipoğlu**,* Bilkent University, Turkey*; C. Yanık,* Sabancı University*; M. Ghavami, M.S. Hanay,* Bilkent University, Turkey

Here, we demonstrate a buckling based, nanoelectromechanical logic bit with high controllability and low logic input voltage. The device consists of a slender beam to store information through its buckling direction and a comb-drive structure for initiating buckling electrostatically. When an actuation voltage is applied to the fingers of the comb-drive structure, an axial compressive force is applied to the suspended slender beam which is connected to an anchor from the opposite end. Applied axial force creates a compressive stress on the slender beam which leads to buckling after a critical load. Buckling direction can be controlled (left/right) by changing the applied side-gate control voltages. The capacitive attraction force generated between the beam and the activated electrode controls the direction of the buckling. Control voltage acts as the logic input for writing information and it is only required just before the application of the axial load, so that the beam can be preloaded to the target direction. Lateral deformations as large as 10% of the beam length can be achieved.

Once the beam is buckled to the desired direction, the removal of the guidance voltage does not affect the buckling state of the beam, which indicates successful non-volatile information storage. Moreover, by altering the voltage difference created in the comb-drive structure, buckling amount can be controlled very precisely. Control voltages as low as 0.5V are demonstrated for storing information. The device is fabricated from an SOI wafer by using electron beam lithography, metal deposition and plasma / HF etching techniques. The dimensions of the slender beam are 150nm x 250nm x 40µm for the width, thickness and length respectively. Several videos demonstrating dynamically controlled electrostatic buckling have been recorded during the experiments. The nanoelectromechanical logic memory demonstrated here is scalable since its operation does not require any high-end electronic instruments such as function generators, and can be accomplished by simply using DC power sources. To readout the state of the beam all-electronically, the device is capacitively coupled to a microwave resonator. The changes in the frequency shows clear transitions between buckled and straight states.

It is possible to build two-bit mechanical logic gates and more involved logic units by using proposed nanoelectromechanical logic bit. As a further matter, precise control of the buckling in nanoscale can be very promising for demonstrating the interconnection between information science and thermodynamics.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+2D+AS+MN+PC-ThA

SPM – Probing Electronic and Transport Properties

Moderators: Ondrej Dyckoe, Oak Ridge National Laboratory, Sergei Kalinin, Oak Ridge National Laboratory, Indira Seshadri, IBM Research Division, Albany, NY

2:20pm **NS+2D+AS+MN+PC-ThA1 Imaging Currents in Two-dimensional Quantum Materials*, Katja Nowack,*** Cornell University **INVITED**

Magnetic imaging is uniquely suited to the non-invasive imaging of current densities, particularly in two-dimensional devices. In this talk, I will showcase this approach by discussing measurements on HgTe quantum well devices in the quantum spin Hall (QSH) regime. In a nutshell, we scan a superconducting quantum interference device (SQUID) to obtain maps of the magnetic field produced by the current flowing in a device. From the magnetic image we reconstruct a two-dimensional current distribution with a spatial resolution on the micron scale. This allows us to directly visualize that most of the current is carried by the edges of the quantum well devices when tuned into their insulating gaps - a key feature of the QSH state. I will both discuss routes towards improving the spatial resolution of our measurements to sub-micron length scales through a combination of improved image reconstruction and smaller sensor sizes.

3:00pm **NS+2D+AS+MN+PC-ThA3 Side-gate Construct for Probing Active Energy Levels in Electron Transport through a Solid-state Surface-bound Protein Monolayer*, Sidney Cohen,*** *B. Kayser, C. Gua, M. Sheves, I. Pecht, D. Cahen,* Weizmann Institute of Science, Israel

Electron transport studies provide an excellent platform to deduce electronic structure in molecular electronics studies, enabling control and understanding of the pathways and mechanisms involved. Due to their complexity, proteins are used only infrequently in this context, despite convenient properties such as selective binding, self-assembly, light sensitivity, and the possibility to (bio) chemically tailor properties . Here, we study electron transport in monolayer films of Azurin, using a 3-electrode configuration with a novel side-gate. The source and drain are gold substrate and conductive atomic force microscope (C-AFM) probe, respectively. The measuring devices were prepared in a two-step electron beam lithography process, whereby interdigitated drain and gate electrodes with separation of 80 nanometers are patterned from macroscopic electrodes, the latter formed optically on a silicon oxide substrate. The gold electrodes are patterned with the gate elevated by 20 nm for improved coupling with the drain. After deposition of the Azurin monolayer on this structure, the carrier chip was wire-bonded for insertion into the AFM. Azurin was incorporated in the device both as copper-containing holo-Azurin, and as apo-Azurin with the Cu ion removed. Stability of source-drain vs. $V_{source-drain}$ curves, as well as gate-drain leakage were monitored for validity. $I_{source-\ drain}$ vs. $V_{source-drain}$ curves were acquired at different gate voltages, and $I_{source-\ drain}$ at 0 $V_{source-drain}$ was measured while sweeping V_{gate} in both polarities. Asymmetry of current onset for opposing gate biases points to a low-lying LUMO transport level for holo-Azurin. For apo-Azurin this level is shifted to higher values and hence inaccessible. Semi-quantitative location of the tail of this LUMO, as well as value of gate coupling were estimated by changing the work function of the drain electrode, i.e. C-AFM probe, from Pt (ϕ=-5.3 eV) to Au (ϕ= -4.9 eV). The observations can be rationalized by considering previous electrochemical and theoretical studies.

3:20pm **NS+2D+AS+MN+PC-ThA4 Adding Electrons One at a Time to Electrostatically Confined Graphene Quantum Dots*, Daniel Walkup,*** *C. Gutierrez, F. Ghahari,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; C. Lewandowski,* MIT*; J. Rodriguez-Nieva,* Harvard University*; T. Taniguchi, K. Watanabe,* National Institute for Materials Science (NIMS), Japan*; L. Levitov,* MIT*; N.B. Zhitenev, J.A. Stroscio,* National Institute of Standards and Technology (NIST)

The Coulomb blockade of adding charges to isolated metallic systems is one of the most characteristic phenomena of quantum dots (QDs). Here, we created circular graphene QDs in a backgated graphene-hexagonal boron nitride (hBN) device by locally ionizing defects in the hBN layer, using the electric field from the tip of a scanning tunneling microscope (STM). Scanning tunneling spectroscopy (STS) enables us to image the local density of states outside and within these circular graphene resonators. At weak magnetic fields, confinement of graphene electrons is poor and Coulomb blockade is not observed. At higher fields, however, the graphene electrons form quantized Landau levels (LLs) separated by energy gaps. In the area of the QD, the LLs are bent by the electrostatic potential creating metallic (compressible) rings where a LL crosses the Fermi energy, separated by circular insulating barriers (incompressible strips), which isolate the dot from the graphene and enable the onset of Coulomb blockade. Tunneling dI/dV spectra inside the QD reveal a series of Coulomb blockade peaks, which shift as a function of back gate voltage. In the plane defined by gate voltage and sample bias, these peaks form Coulomb lines, whose slope is governed by the relative capacitances between the dot, tip, gate, and sample bias electrodes, and whose relative offsets reveal the addition spectrum of the quantum dot. A characteristic feature of the Coulomb blockade in these systems is the presence of different families of charging lines, one for each LL, which intersect each other and experience avoided crossings. The avoidance pattern of these anticrossings is novel: at the strongest fields, it somewhat resembles the predictions of simple models of electrostatically-coupled QDs, but at weaker fields it diverges very strikingly, and new modeling is needed to reproduce it. This avoidance pattern reflects the interaction of electrons in different LLs, occupying different parts of the QD, and is tunable via the magnetic field and gate voltage. By moving the STM tip, we can tune the tip-dot capacitance, and tunnel into different parts of the dot, enabling a full characterization of the anticrossings in these novel electronic nanostructures.

4:00pm **NS+2D+AS+MN+PC-ThA6 Bulk and Surface Contribution to the Charge and Spin Transport in Topological Insulators Observed with a Four-Probe Scanning Tunneling Microscope*, Wonhee Ko,*** *G.D. Nguyen,* Oak Ridge National Laboratory*; H. Kim, J.S. Kim,* Pohang University of Science and Technology, Republic of Korea*; A.-P. Li,* Oak Ridge National Laboratory

Topological insulators are fascinating materials for future electronics because of its superior charge and spin transport characteristics stemming from their topological nature. However, topological insulators realized in actual materials have both bulk and surface carriers, where the former significantly hampers the topological transport of the later. In this talk, we utilize four-probe scanning tunneling microscope to investigate bulk and surface contribution to the charge and spin transport in bulk-insulating topological insulator Bi_2Te_2Se. The relative contribution of bulk and surface was varied by changing temperature and transport area, which was measured by variable probe-spacing spectroscopy. The surface dominant regime was already reached at 82 K, where the sample exhibited superior transport properties such as a large surface mobility and high spin polarization. At this regime, the contact to external probes also transforms from Schottky to Ohmic junction. Our result indicates that controlling bulk and surface contribution to the transport is crucial for realizing topological devices.

4:20pm **NS+2D+AS+MN+PC-ThA7 Modulation of Single-Walled Carbon Nanotube Electronic Structure by External Electronic Perturbations: Scanning Tunneling Spectroscopy and Density Functional Theory*, Benjamen Taber*[1]**, *G.V. Nazin,* University of Oregon

Understanding the local impact of environmental electronic perturbations on the local density of states (LDOS) of single-walled carbon nanotubes (CNTs) is critical for developing CNT-based devices. We present scanning tunneling microscopy and spectroscopy (STM/STS) investigations of CNTs adsorbed on both a metal, Au(111), and a dielectric, monolayer RbI on Au(111), serving as models for stronger and weaker electrostatic interactions, respectively. In both cases, STS revealed modulations in the CNT LDOS corresponding to features in the underlying material. We then corroborate our STM/STS results with density functional theory calculations of the electronic structure of semiconducting CNTs in the presence and absence of an external dipole (a pair of opposite charges). DFT-calculated CNT LDOS quantitatively matched STM/STS results, providing key insight in to the local impact external charges have on CNT electronic structure.

4:40pm **NS+2D+AS+MN+PC-ThA8 Single Charge and Exciton Dynamics probed on the Molecular Scale*, Anna Roslawska,*** *P. Merino, C. Grosse, C.C. Leon, O. Gunnarsson, M. Etzkorn, K. Kuhnke, K. Kern,* Max Planck Institute for Solid State Research, Germany

The performance of organic optoelectronic devices depends on the dynamics of charges and excitons (electron-hole pairs). The relevant processes have been mostly studied by time-resolved techniques with a

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[1] **NSTD Postdoc Finalist**

spatial resolution limited by optical diffraction. In order to overcome this limit, a nanoscale scanning probe approach that enables addressing individual light emitters is preferred. Here we introduce time-resolved scanning tunneling microscopy-induced luminescence (TR-STML) and use it to explore locally the single charge and single exciton regime. The excitonic light originates from structural defects in C_{60} thin films on Au(111) that act as charge and exciton traps. Such a defect is a single photon emitter, whose spectrum has a sharp electron-hole recombination feature [1,2]. By measuring the time-resolved electroluminescence due to individual injected charges, it is possible to analyze the formation and recombination processes of single excitons and determine their characteristic time constants[3].

[1] P. Merino, C. Große, A. Rosławska, K. Kuhnke, K. Kern, , Nat. Commun., 6, 8461, 2015.

[2] C. Große, P. Merino, A. Rosławska, O. Gunnarsson, K. Kuhnke, K. Kern, ACS Nano, 11, 1230-1237, 2017.

[3] A. Rosławska, P. Merino, C. Große, C. C. Leon, O. Gunnarsson, M. Etzkorn, K. Kuhnke, K. Kern, arXiv:1803.10088.

5:00pm **NS+2D+AS+MN+PC-ThA9 Microscopic Understanding of the Temperature-dependent Carrier Transport in Ge Nano - Crystal s Films***, Dan Shan,* Yangzhou Polytechnic Institute, China*; J. Xu,* Nanjing Universityy, China

Silica-based semiconductor nano-crystals have attracted much interest in recent years due to their possible applications in many kinds of nano-electronic and optoelectronic devices. Compared with Si, Ge has larger electron and hole mobility. Furthermore, Ge has a narrower band-gap and high phonon responsivity in the near-infrared region, so it is suited to many near-infrared applications. In order to further improve the device performance, detailed knowledge of transport mechanisms across these nano-crystals becomes necessary and is considered indispensable.

In this work, hydrogenated amorphous germanium films were prepared by a plasma enhanced chemical vapor deposition technique. Ge nano-crystals (Ge NCs) films were obtained by thermal annealing the as-deposited samples. P-type behavior in Ge NCs films without any external doping is attributed to the holes accumulation caused by acceptor-like surface states. It can be found that the dark conductivity and Hall mobility reach to as high as 25.4 S/cm and 182 $cm^2/V \cdot s$ in the Ge NCs film, which are much higher than the previously reported data. Carrier transport mechanisms of Ge NCs films were investigated by temperature-dependent Hall measurement. Three kinds of temperature-dependent conductivity behaviors, which exhibit the linear relationships of the ln σ versus $T^{-1/4}$, $T^{-1/2}$ and T^{-1}, respectively, were observed in the temperature regions of 10-500 K. It can be confirmed that the thermal activation conduction in the extended states dominated the carrier transport process above 300 K (300-500 K). Below room temperature, the carrier transport process was dominated by the percolation-hopping conduction at 90-230 K and turned to Mott-VRH conduction when the temperature falling below 50 K (10-50 K).

Furthermore, the different scattering mechanisms in carrier transport process were found in different temperature regions, which were evaluated via temperature-dependent Hall mobilities. In the low temperature region (10-50 K), the carrier Hall mobility is almost temperature independence ($\mu \sim T^0$), revealing the neutral impurities' scattering mechanism dominated the carrier transport process. When increasing the temperature (50-190 K), the carrier transport properties were controlled by the grain boundary scattering mechanism, where the carrier Hall mobility was increased with temperature and exhibited the thermally activated behavior. However, the relationship of $\mu \sim T^{-0.9}$ was observed above room temperature (300-500 K). It is suggested that the carrier transport is dominated by a superposition of grain boundary scattering and acoustic phonon scattering within the high temperature region.

Plasma Science and Technology Division
Room 104C - Session PS+EM+TF-ThA

Atomic Layer Processing: Integration of ALD and ALE
Moderator: Scott Walton, U.S. Naval Research Laboratory

2:20pm **PS+EM+TF-ThA1 Atomic-Layer Etching (ALE) of Nickel or Nickel Oxide Films by Hexafluoroacetylacetone (HFAC) Molecules***, **Abdulrahman Basher**, M. Isobe, T. Ito, K. Karahashi,* Osaka University, Japan*; M. Kiuchi,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; T. Takeuchi,* Nara Women's University, Japan*; S. Hamaguchi,* Osaka University, Japan

Atomic layer etching (ALE) is one of the most promising technologies and a prospective solution to various technical problems in nanometer-scale device fabrication processes. ALE consists of a series of processing cycles and, in each cycle, a transition step to form a reactive thin layer on the material surface is followed by a removal step to take off only this modified layer. For a metallic film, the formation of volatile organic metal complexes may be used to establish low-damage ALE processes. In this study, to explore the possibility of establishing new etching processes for the manufacturing of magnetoresistive random access memories (MRAMs), we examine possible etching reactions of magnetic materials with organic molecules. In this study, we select Ni as a sample of ferromagnetic materials. An earlier studies [1,2] indicated that hexafluoroacetylacetone (hfac) may be used for etching of Ni due to the possible formation of nickel(II) hexafluoroacetylacetonate $Ni(hfac)_2$. According to [2], if a Ni surface is oxidized and then exposed to gas-phase hfac, $Ni(hfac)_2$ are formed when the substrate temperature is increased. It is pointed out that, without the oxidation process, $Ni(hfac)_2$ is not formed under similar conditions. Therefore, the expected single cycle of Ni ALE by gas-phase hfac is as follows; a Ni surface is first exposed to oxygen and then to hfac. This step is then followed by the increase of substrate temperature. In this study, however, the goal of this study is to understand the interaction mechanisms between hfac and a Ni or NiO surface and we use the first principles calculation to examine the interaction of a hfac molecule with a Ni or NiO surface atoms. The simulation results based on Gaussian 09 that we have obtained so far suggest that the transfer of a proton from an enol hfac molecule to the Ni or NiO surface generates its deprotonated anion, whose oxygen atoms strongly interact with a positively charged Ni atom on the surface and thus form a precursor of a highly volatile metal complex. Difference in charge distribution between Ni and NiO surfaces affects the likelihood of the formation of such precursors. Surface roughness may also affect such surface reactions.

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[1] Chen J. K., Altieri N. D., Kim T., Chen E., Lill T., Shen M., and Chang J. P., " Direction etch of magnetic and noble metals. II. Organic chemical vapor etch," *J. Vacuum Sci. & Tech. A***35**, 05C305 (2017).

[2] Nigg H. L. and Masel R. I., " Surface reaction pathways of 1,1,1,5,5,5-hexafluoro-2,4-pentandione on clean and pre-oxidized Ni(110) surface," *J. Vacuum Sci. & Tech. A***17**, 3477 (1999)

2:40pm **PS+EM+TF-ThA2 Thermal Atomic Layer Etching of HfO_2 Using HF for Fluorination and $TiCl_4$ for Ligand-Exchange***, Y. Lee, **Steven George**,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) can be accomplished using sequential fluorination and ligand-exchange reactions. HF has been a typical fluorination reactant. Various metal precursor s have been used for ligand-exchange such as $Sn(acac)_2$, $Al(CH_3)_3$ and $AlCl(CH_3)_2$ and $SiCl_4$. This study explored $TiCl_4$ as a new metal chloride precursor for ligand-exchange. Thermal HfO_2 ALE using $TiCl_4$ and HF as the reactants was studied using *in situ* quartz crystal microbalance (QCM) measurements from 200 - 300 °C. The HfO_2 films were etched linearly versus number of $TiCl_4$ and HF reaction cycles. The sequential $TiCl_4$ and HF reactions were also self-limiting versus reactant exposure. The QCM studies observed a mass change per cycle (MCPC) of -10.2 ng/(cm^2 cycle) at 200 °C and -56.4 ng/(cm^2 cycle) at 300 °C. These MCPCs correspond to HfO_2 etch rates of 0.11 Å/cycle at 200 °C and 0.59 Å/cycle at 300 °C. To explore the selectivity of thermal ALE using $TiCl_4$ and HF as the reactants, spectroscopic ellipsometry (SE) measurements were also employed to survey the etching of various materials. The SE results revealed that HfO_2 and ZrO_2 were etched by $TiCl_4$ and HF. In contrast, Al_2O_3, SiO_2, Si_3N_4, and TiN were not etched by $TiCl_4$ and HF. QCM studies also revealed that $TiCl_4$ and HF were able to etch Ga_2O_3. The etching selectivity can be explained by the reaction thermochemistry and the stability and volatility of the possible etch products. Al_2O_3 can also serve as an etch stop for HfO_2 ALE.

3:00pm **PS+EM+TF-ThA3 Rapid thermal-cyclic Atomic Layer Etching of SiO_2 Using Infrared Annealing***, **Nobuya Miyoshi,*** Hitachi High-Technologies, Japan*; H. Kobayashi, K. Shinoda, M. Kurihara,* Hitachi, Japan*; K. Kawamura, K. Ookuma, Y. Kouzuma, M. Izawa,* Hitachi High-Technologies, Japan

Device structures are changing from planar-types to three-dimensional types, such as fin-type field-effect transistors and gate-all-around transistors, in order to reduce leakage current and power consumption. Furthermore, fabricating these devices requires both high selectivity and precise control of device dimensions below the 10 nm scale. Atomic layer etching (ALE), which involves the layer-by-layer removal of thin films, is expected to meet these requirements. In a conventional ALE process for SiO_2[1], HF and NH_3 molecules are exposed to the surface simultaneously. In this case, the etching amount per cycle is proportional to square root of the exposure time of HF and NH_3, indicating that the process is quasi-self-limiting (not self-limiting).

We have been investigating a thermal ALE of SiO_2 in which ammonium fluorosilicate-based surface modified layer is formed after exposure to HF and NH_3 gas, and removed by using infrared annealing. Etching depth of blanket SiO_2 samples were measured by using in-situ ellipsometry. We found that self-limiting formation of the modified layer was achieved with separate exposure of HF and NH_3 gas. In addition, we successfully demonstrated that this etching process was highly selective with respective to poly-Si and SiN. Comparison between experimental results and Langmuir adsorption model for dependence of etching rate on partial pressure of HF and NH_3 clarified that the SiO_2 surface during the gas exposure is in adsorption-desorption equilibrium.

In addition to HF/NH_3 gas chemistry, we developed an ALE process utilizing plasma to generate HF molecule in stead of using HF gas. This process consists of plasma discharge for HF exposure, evacuation of the residual gas, NH_3 exposure, and infrared annealing. In the plasma discharge, fluorine based gases, such as CF_4, NF_3, and SF_6 were diluted by H_2 gas. The etching rate of SiO_2 saturated at 2.8 nm/cycle in regard to the discharge time, which indicates self-limiting behavior of the modification step. In contrast, the etching rates of poly-Si and SiN were below the detection limit of in-situ ellipsometry, demonstrating that this etching process for SiO_2 is highly selective to poly-Si and SiN.

[1] H. Nishio, et al., J. Appl. Phys. **74**, 1345 (1993).

3:20pm **PS+EM+TF-ThA4 The Smoothing Effect in Atomic Layer Etching (ALE)***, **Keren Kanarik**, S. Tan, W. Yang, I.L. Berry, T.B. Lill, Y. Pan, R.A. Gottscho,* Lam Research Corporation

Since the 1970s, the semiconductor industry has fabricated electronic circuits using a pattern-transfer approach that is remarkably reminiscent of the etching artform used centuries ago. Only, now, the patterns are a million times smaller, and require etching to within a few atoms on features less than 40 atoms wide. The most advanced etching technique in production today is called atomic layer etching (ALE). To the extent that an ALE process behaves ideally – with high ALE synergy and self-limiting behavior – the primary benefit is improved uniformity across all length scales: at the surface, between different aspect ratios, and across the full wafer. The focus here will be on the atomic-scale topography of the surface left behind after etching.

The purpose in this presentation is to introduce a new ALE benefit – the smoothing effect. By this, we mean that, beyond maintaining surface topography, ALE can improve the surface smoothness (ref 1). We will show that the effect in directional ALE is pervasive across different material systems, including Si, C, Ta, and Ru. We will propose explanations for the ALE smoothing phenomenon, and identify possible applications for this effect both inside and outside the semiconductor industry.

Ref 1: Kanarik, Tan, and Gottscho. *J. Phys. Chem. Rev.* submitted April 1, 2018.

4:00pm **PS+EM+TF-ThA6 Prospects for Combining ALD and ALE in a Single Chamber***, **Mike Cooke,*** Oxford Instruments, UK **INVITED**

There are obvious similarities between the process cycles of atomic layer deposition (ALD) and atomic layer etching (ALE), so could one machine do both? It is already the case that plasma enhanced chemical vapour deposition (PECVD) tools also perform etching, for the purpose of chamber cleaning. Deposition can also be performed in a tool configured for plasma etching, whether accidentally by creating a plasma with net deposition of fluorocarbon polymer, or by deliberately introducing gases such as silane. However, the wafer is usually heated above ambient in the range 100C – 400C for deposition, in both parallel plate PECVD and when using a high density plasma, while the wafer is typically cooled for etching.

There are also clear overlaps between the hardware requirements for atomic layer deposition and thermal atomic layer etching. The overlaps are more restricted for plasma enhanced ALD and ALE, because both the wafer temperature range and the character of the plasma can differ. In ALD there are benefits from using a remote plasma, because the plasma primarily creates a flux of radicals, while in ALE the plasma delivers both radicals and an ion bombardment flux. However, there is potential for combining plasma ALD and ALE in a chamber with an RF biased table. Thermal ALE and plasma ALE can be combined if the wafer table has a wide temperature range, and the tool can deliver doses of low vapour pressure ALE precursors.

The motivation for combining processes is less clear outside the academic community. Researchers wanting to access both precision etching and deposition under tight constraints of space and budget may be attracted to it, but the combination of halogen chemistry for ALE and organometallic precursors for ALD may make it difficult to change quickly between etching and deposition.

Results from ALE and ALD are presented to explore the overlap, including recent work on ALE and ALD for III-V power devices.

4:40pm **PS+EM+TF-ThA8 Low Temperature Surface Preparation of GaN Substrates for Plasma Assisted-Atomic Layer Epitaxial Growth***, **Samantha G. Rosenberg,*** U.S. Naval Research Laboratory*; D.J. Pennachio,* University of California, Santa Barbara*; M. Munger,* SUNY Brockport*; C. Wagenbach,* Boston University*; V.R. Anderson,* U.S. Naval Research Laboratory*; S.D. Johnson,* U. S. Naval Research Laboratory*; N. Nepal, A.C. Kozen, J.M. Woodward,* U.S. Naval Research Laboratory*; Z.R. Robinson,* SUNY Brockport*; K.F. Ludwig,* Boston University*; C.J. Palmstrøm,* University of California, Santa Barbara*; C.R. Eddy, Jr.,* U. S. Naval Research Laboratory

We have previously shown that using our low temperature plasma-assisted atomic layer epitaxy (ALEp) method we can grow AlN and InN for various applications.[1-3] The materials we have grown using our ALEp method have shown good crystalline quality, but suffer from an incorporation of carbon. Theory has led us to believe that the substrate preparation plays a significant role in the remediation of carbon, as that surface becomes the interface for the growth of the III-N film. Therefore, using surface science techniques, we strive to develop not only a fundamental understanding of the ALEp growth process but also atomic layer processes that will result in the best preparation method for a pristine GaN starting surface for ALEp.

In-situ surface studies of *in-situ* and *ex-situ* GaN substrate preparation and InN ALEp growth were conducted to advance fundamental understanding of the ALEp process. We conduct *in-situ* grazing incidence small angle x-ray scattering (GISAXS) experiments at the Cornell High Energy Synchrotron Source to investigate growth surface morphological evolution during sample preparation including a gallium-flash-off atomic layer process (ALP) at varying temperatures and number of cycles. GISAXS information is complemented with *in-vacuo* x-ray photoelectron spectroscopy, reflection high-energy electron diffraction, and *ex-situ* atomic force microscopy studies conducted at the Palmstrøm Lab at UCSB, where we consider different *ex-situ* sample preparation methods to produce the most suitable GaN surface for our ALP/ALEp-based approach. We have determined that a combination of UV/ozone exposure followed by an HF dip produces the cleanest and smoothest GaN surface. We have further determined with GISAXS that ALP-based gallium-flash-off experiments performed at higher temperatures (500°C) produce a smoother starting surface than lower temperatures. Additionally we have determined that we should only perform ~10 cycles of ALP gallium-flash-off instead of 30 as was empirically chosen previously. Due to the sensitivity of the GISAXS experiment, we are able to observe the effect of individual components of the ALP process cycle (pulse vs purge), leading us to insights on the underlying chemical process of the gallium-flash-off ALP. Combining these two results, *ex-situ* and *in-situ* cleaning preparation, should lead us to the best GaN starting surface to grow high quality crystalline InN films.

[1] N. Nepal, et al., Appl. Phys. Lett. 103, 082110 (2013)

[2] C. R. Eddy, Jr, et al., J. Vac. Sci. Technol. A 31(5), 058501 (2013)

[3] R. S. Pengelly, et al., IEEE Trans. Microwave Theory Tech. 60, 1764 (2012)

5:00pm **PS+EM+TF-ThA9 Chemical Interactions with Alkali Compounds for Controlling the Transition between Thermal HF-based Atomic Layer Etching and Deposition***, **John Hennessy,*** Jet Propulsion Laboratory, California Institute of Technology

The use of anhydrous hydrogen fluoride (HF) as a precursor can result in a variety of atomic layer deposition (ALD) processes for thin films like MgF_2,

AlF_3 and LiF, with good optical properties in the deep ultraviolet. Cyclic exposure to HF and several organoaluminum compounds including trimethylaluminum (TMA), can also result in the thermal atomic layer etching (ALE) of some oxide films like Al_2O_3. In this work we show that the introduction of alkali halide compounds (such as LiF or KBr) into the reactor during this cyclic exposure can dramatically alter the deposition and etch conditions at a given substrate temperature. This occurs via the formation of an intermediate complex between the metalorganic precursor and the alkali compounds, that then enhances the removal of the surface fluoride created during the preceding HF exposure. Although the etch rate can be enhanced via this interaction at a given substrate temperature, the process remains self-limiting overall.

This approach provides a pathway to the low temperature (~100 °C) thermal ALE of Al_2O_3. This can be useful for substrate-sensitive applications where exposure to high temperature or energetic plasmas is undesirable. The interaction of TMA and the alkali halide also results in approaches for the spatially-selective deposition of AlF_3, or the spatially-selective etching of Al_2O_3.

We have utilized this combination of ALE and ALD to gently remove the native oxide from metallic aluminum and replace it with AlF_3 for a variety of optics and sensing applications at JPL. This can be performed by variation of the substrate temperature to switch continuously from ALE-mode to ALD-mode, or by variation of the aluminum precursor to tune the chemical interactivity with the alkali compounds. Fabricated devices made with this concept are relevant for a variety of NASA astrophysics and planetary science applications at ultraviolet wavelengths.

5:20pm **PS+EM+TF-ThA10 Selective Processing to Enable High Fidelity Control for the 5 nm Node***, **Benjamen Rathsack,*** Tokyo Electron America, Inc.*; A. Ranjan,* TEL Technology Center, America, LLC.*; P.L.G. Ventzek,* Tokyo Electron America, Inc.*; H. Mochiki,* Tokyo Electron Miyagi, Ltd., Japan*; J. Bannister,* Tokyo Electron America, Inc. **INVITED**

Selective processing through the integration of Etch and ALD is critical to enable high fidelity control for 5 nm node structures. The complexity of multi-step integrations and processes has caused edge placement error (EPE) to become a critical challenge. The enablement of further scaling requires the utilization of self-aligned processing to address overlay variation as well as highly selective processing to address localized fidelity control. Fidelity control has become complex on multi-step processes integrated for SAQP, self-aligned block (multi-color) and high-aspect ratio structures. Localized fidelity control is highly dependent on both the material stacks and selective processing capabilities. This includes stringent selectivity, profile, loading and uniformity requirements. To meet these requirements, the fusion of Etch and ALD enables atomic level precision with minimal impact from CD loading effects. The fusion of Etch and ALD processing also improves across wafer CD control and LWR. The use of selective processing is demonstrated to be a key enabler of 5 nm node fidelity control.

Plasma Science and Technology Division
Room 104A - Session PS-ThA

Plasma Diagnostics, Sensors and Controls

Moderator: Steven Shannon, North Carolina State University

2:20pm **PS-ThA1 In-situ Measurement of Electron Emission and Electron Reflection Yields***, **Mark Sobolewski,*** National Institute of Standards and Technology (NIST)

Bombardment of plasma-exposed surfaces by energetic particles causes electrons to be emitted, which in turn influence the plasma. Accurate plasma simulations require knowledge of the flux or yield of emitted electrons. Yields can be measured directly in beam studies, but it is impractical to produce a beam of each possible energetic particle produced by typical plasmas. In contrast, in-situ measurements, performed during plasma exposure, provide useful values for effective or total electron emission yields, summed over all the energetic particles present for given plasma conditions. Here, measurements were performed at 5-10 mTorr in a radio-frequency (rf) biased, inductively coupled plasma (icp) system. The rf voltage and current across the sheath adjacent to the rf-biased electrode are measured, along with Langmuir probe measurements of ion current density and electron temperature. The measurements are analyzed by a numerical sheath model, which allows the current of electrons emitted from the surface to be distinguished from other mechanisms of current flow. An insulating cap placed on the rf-biased electrode exposes a small, off-center portion of its area. The cap, combined with the azimuthal electric field generated by the icp source, allows outgoing, emitted electrons to be distinguished from electrons reflected at the counterelectrode surface. Thus we obtain values for the total yield or flux of electrons emitted at the rf-biased surface and the reflection coefficient at the counterelectrode. The technique is validated by comparing measurements made in argon discharges with literature results and then is applied to characterize yields at practical surfaces in inert gas plasmas and fluorocarbon etching plasmas.

2:40pm **PS-ThA2 Electron Energy Distribution Measurements in Dusty Non-thermal Plasmas***, **Austin Woodard**, L. Mangolini,* University of California, Riverside

Dusty plasmas are a peculiar class of plasmas characterized by the presence of charged solid particles. Understanding the properties of these environments, ever-present in laboratory discharges, represent a crucial requirement for the engineering and optimization of several plasma-based processes employed in industrial manufacturing, such as thin film fabrication and etching. Langmuir probe measurements represent a well-established method used for the investigation of the properties of plasma discharges, such as the electron density, the ion density, the electron temperature and the electron energy distribution function (EEDF). In dust-rich plasmas, however, the application of the Langmuir probe method is quite challenging as the dust particles quickly form an insulating film on the probe surface which may hinder a reliable measurement. In this contribution, Langmuir probe measurements are performed in an inductively coupled RF Ar-H_2 primary plasma which is dosed with conductive nanoparticles produced in a secondary RF plasma reactor. To avoid the formation of an insulating coating, graphitic carbon nanoparticles, obtained in the secondary reactor from the dissociation of C_2H_2 in an Ar-H_2 plasma, are used for this study. The conductive graphitic nanoparticle coating formed on the probe tip does not negatively impact EEDF measurements in a pristine Ar-H_2 plasma, allowing a more forgiving environment in which to study the effect of dust on plasma properties. The EEDF is obtained through the Druyvesteyn method, via the second-derivative of I-V probe characteristics. Electron densities and temperatures are obtained from the EEDF measurements, while ion densities are calculated from the I-V characteristics. The role of process parameters such the nanoparticle density and the primary plasma input power is carefully mapped. The nanoparticle density is measured through the mass injection rate into the primary reactor, allowing for the particle charge to be measured across the parameters. In the dust-free pristine Ar-H_2 plasma, a transition in the primary ion is observed as a function of the applied RF power: H_3^+ appears to dominate at low powers, transitioning to Ar^+ at higher values. In dusty environments, the measured plasma power is much lower than in pristine, prompting H_3^+ as a likely choice for the primary ion in ion density calculations. As expected from theory and previous literature, nanoparticles act as electron sinks, reducing the electron density inside the plasma volume, resulting in an increased electron temperature to maintain ionization events; contrary to theory, however, the electron temperature increases with increasing input plasma power.

3:00pm **PS-ThA3 The Surface Plasmon Energy and the Secondary Electron Emission on an Oxidized Aluminum Surface***, J.-T. Li, J. Qiu, **Yi-Kang Pu**,* Tsinghua University, China **INVITED**

The energy evolution of surface plasmons and the apparent secondary electron yield on an aluminum surface during the oxidation process are investigated in an experiment under a controlled environment. The surface plasmon energy is determined from the location of the surface plasmon loss peak in the EELS spectra; at the same time, the total oxygen coverage (in the submonolayer regime) and the oxide layer thickness (in the multilayer regime) are obtained from the peak profiles of O 1s and Al 2p photoemission lines in the XPS spectra. The apparent secondary electron yield is deduced from the breakdown voltage between two parallel plate electrodes in a 360 mTorr argon environment using a Townsend breakdown model. In the submonolayer regime, both the surface plasmon energy and secondary electron yield decrease with the total oxygen coverage. In the multilayer regime, the surface plasmon energy continues to decrease with the oxide layer thickness although the rate of decrease is lower. However, the secondary electron yield sharply increases with the oxide layer thickness. In this presentation, we will discuss possible mechanisms for the variation of these quantities and compare the measured results with that from the models.

4:00pm **PS-ThA6 Transient Phenomena in Power Modulated Chlorine Plasma***, **Priyanka Arora**, T. List, T. Ma,* University of Houston*; S. Shannon,* North Carolina State University*; S. Nam,* Samsung Electronics Co., Ltd., Republic of Korea*; V.M. Donnelly,* University of Houston

Power-modulated plasmas (i.e. rapid switching from high to low power) could have some potential advantages over conventional pulsed plasmas (where power is periodically turned completely off) for plasma processing in that a larger parameter space is available between fully pulsed and continuous power. In the present study, power at 13.56 MHz applied to a mostly chlorine inductively-coupled plasma was modulated between a high power and low power state. Time-resolved optical emission, Langmuir probe, and forward and reflected power measurements were performed. Two distinct types of transient phenomena were found upon switching from the high power to low power state. In a "normal" mode, electron temperature (T_e) remains constant, while electron and ion number densities (n_e and n_i^+) and optical emission intensities smoothly drop to a level roughly equal to the fractional drop in power. In a second "anomalous" mode, n_e, T_e and optical emission intensities rapidly drop and stay low for an extended period before rising to values commensurate with the drop in power. Under many circumstances, a single delay time is found that depends on pressure and power duty cycle. In some cases, two delay times can be found, with subtle changes in matching network settings causing one delay time or the other. The anomalous mode can exhibit complex behavior such as two or three phases in the low power period, and periodicity at half the pulsing frequency. The anomalous mode will be discussed in terms of negative ion-driven instabilities.

4:20pm **PS-ThA7 Measurements of RF Magnetic Fields and Plasma Current in Coupled Low and Very High Dual-Frequency Plasma Sources***, J.P. Zhao, P.L.G. Ventzek, B. Lane,* Tokyo Electron America, Inc.*; **Toshihiko Iwao**, K. Ishibashi,* Tokyo Electron Technology Solutions Ltd., Japan

Plasma processing systems capacitively driven at very high frequencies (VHF, e.g. 100MHz) have attracted much interest for semiconductor and flat panel display processing. VHF has the advantage of generating plasma with more efficiency as power is coupled more into electrons and less into ions in the sheath. Benefits are seen for processes requiring reduced ion energy, ostensibly to minimize damage, high ion and radical flux to the substrate. The benefits of VHF are accompanied by challenges. The short wavelength associated with VHF power is reduced even further in the presence of high density plasma. The wavelengths are comparable to the RF electrode dimension. As a result, spatial variations in plasma density and sheath voltage can arise and lead to undesired non-uniformities in process parameters. Skin effects associated with high plasma density and plasma-sheath local resonances are other destroyers of plasma uniformity. Previously, we have reported[1] a detailed investigation on the spatial and temporal evolution of RF magnetic field and plasma current in a 100MHz plasma source performed with a magnetic field probe (B-dot loop). The probe translated across the diameter of the VHF plasma measured the magnitude and phase of the fundamental and harmonics of the plasma excitation frequency as a function of radial position. The measured magnetic fields displayed a transition from simple to complex behaviors depending on plasma conditions. The spatiotemporal resolved magnetic field exhibits a series of fast current reversals and subsequent circulation driven by inward wave propagation that are electromagnetic in nature. We showed how the onset, frequency and amplitude of the current reversal and subsequent circulation were strongly related to applied plasma conditions. We also showed that plasma current derived from the magnetic field distribution was closely correlated to the plasma density profile measured by a plasma absorption probe. In order to further understand these fundamental electromagnetic structures in VHF plasma, in the current study, we apply LF on top of the VHF aimed to modify the electromagnetic structures. Performed with B-dot probe, we report the spatial and temporal evolution of VHF magnetic field and plasma current as a function of different LF phases as well as the detailed correlation of VHF electromagnetic structure and the LF modulated plasma sheath variation. We show that the coupling of the VHF electromagnetic field to the plasma strongly depends on the phase of the LF driven source. Measurements are compared against different theories for how the VHF power couples to the plasma.

[1] PS+VT-ThA12, 64th AVS Symposium, Tampa FL

4:40pm **PS-ThA8 Self-neutralized Nearly Monoenergetic Positive Ion Beam Extracted From a Pulsed Plasma***, **Ya-Ming Chen**, R. Sawadichai,* University of Houston*; S. Tian,* Lam Research Corporation*; V.M. Donnelly, D.J. Economou, P. Ruchhoeft,* University of Houston

Space charge neutralization of an ion beam extracted from a plasma is crucial for advanced plasma processes which require precise control of the ion flux and the width of the ion energy distribution (IED). In previous studies, filaments thermionically emitting electrons were used for neutralizing the space charge, which would otherwise cause the ion beam to diverge owing to Coulomb explosion.[1, 2] However, the performance of the neutralizing filaments is restricted by their limited lifetime and required extra power supplies. This work reports that a self-neutralized positive ion beam can be extracted from a pulsed plasma. In particular, a nearly monoenergetic ion beam was realized by applying a synchronous DC bias in the afterglow (plasma-off) of the plasma. A mechanism of the self-neutralization process is proposed based on space-time resolved ion and electron current (I_i and I_e) measurements done by a movable Faraday cup. The measurements revealed that electrons from a low-density plasma immediately downstream of the ion extraction grid neutralize the space charge in the beam transport region. Time-resolved plasma potential measurements suggest that there could be two periods for low-energy ions and electrons to leave the source and form the low-density plasma in the downstream of the ion extraction grid. Among the observations are 1) with increasing distance, d, from the grid $I_e > I_i$ at d = 1-5 cm, $I_e = I_i$ at d ≈ 20 cm, and $I_e << I_i$ at d > 30 cm; 2) I_i decays by less than $1/r^2$; 3) electron energy peaks at ~30 eV, ascribed to acceleration by the 100 eV ion beam transiting through the downstream plasma. Ion flux and IEDs were also studied using a retarding field energy analyzer (RFEA). Detailed explanations for the self-neutralization process will be described.

Work supported by NSF.

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15 (4), 1853-1863 (1997).

5:00pm **PS-ThA9 Diagnostics of Plasma Neutral Species in a Very High Frequency Oxygen Plasma with High Sensitivity Broadband Absorption Spectroscopy***, **Jianping Zhao**, P.L.G. Ventzek, B. Lane,* Tokyo Electron America, Inc.*; T. Iwao, K. Ishibashi,* Tokyo Electron Technology Solutions Ltd., Japan*; J.-P. Booth,* CNRS, Ecole Polytechnique, France

As advanced memory and logic critical dimensions shrink and stack complexity, film quality and yield requirements increase, precision plasma processes including plasma enhanced atomic layer deposition (PEALD) and atomic layer etch (ALE) experience more demand. Ideally infinite selectivity and damage-free process results with sub-angstrom control are sought. Plasma enhanced processes, particularly PEALD rely on plasma generated radicals for much of their perceived benefit. Furthermore, in both atomic layer etch and deposition processes, low or nearly zero energy ions are required. Large-area plasma processing systems capacitively driven at very high frequencies (VHF, e.g. 100MHz) have attracted much interest for semiconductor device and flat panel display processing. VHF has the additional advantage of generating plasma with more efficiency as power is coupled more into electrons and less into ions in the sheath. Benefits are seen for processes requiring reduced ion bombardment energy, ostensibly to minimize damage and high radical flux to the substrate. Unfortunately, it has been a challenge to measure the neutral plasma species of interest. It would be desirable to use plasma absorption spectroscopy to study plasma neutral species because it can provide direct measurement of the absolute densities of species in their ground state as well as vibrational and rotational properties of neutrals. Lack of intense and stable light sources with wide wavelength coverage and the lack of optical aberration-free spectrographs and detectors with true high resolution has rendered plasma absorption spectroscopy impractical as a solution for industry. Emission based diagnostics such as actinometrical methods are far too imprecise. A recent advance, broadband plasma absorption spectroscopy[1] (BPAS) has been proven to be a very practical improvement of plasma absorption spectroscopy with capability to detect absorbance as low as 1×10^{-4}. In order to understand the fundamental plasma chemistry property of VHF plasma, we present here the measurement of the plasma neutral properties with a high sensitivity BPAS technology. Illustrative measurements were performed in a 100MHz plasma source with pure oxygen plasma spanning a wide RF power and pressure range. Vibrational and rotational properties of O_2 molecules are derived from a theoretical fitting to the experimental spectra. Density of O_2 molecule at different vibrationally excited levels are also derived. Effects of VHF power and pressure on these plasma neutral properties are reported.

[1] Mickaël Foucher, Daniil Marinov, Emile Carbone, Pascal Chabert, and Jean-Paul Booth, Plasma Sources Sci. Technol. 24 (2015) 042001

5:20pm **PS-ThA10 Development of the Virtual Metrology Using a Plasma Information Variable (PI-VM) for Monitoring SiO_2 Etch Depth***, **Yunchang Jang**, H.-J. Roh, S. Ryu, J.-W. Kwon, G.-H. Kim,* Seoul National University, Republic of Korea

Advanced process control (APC) has been attracting attention as a technology to enhance process yield and it requires accurate and reliable virtual metrology (VM). Accuracy of VM is determined by how sensitively the input variables reflect the drift and changes of the process environment. Many previous approaches to improve the performance of VM have been focused on development of the statistical methods to select the valuable input variables from the equipment data and additional sensor data such as optical emission spectroscopy (OES) and plasma impedance monitors (PIM). In this study, the noble variables, named plasma information (PI) variables are introduced, which are obtained by phenomenological analysis and they are added into the VM development. Then we evaluated its contribution to improve the accuracy of VM. It notes that PI variables represents the state of etch plasma so it can be used to monitor the variation of process results in plasma-assisted semiconductor fabrication process. Effect of PI variables on improving VM accuracy has been investigated through following conventional (or standard) VM development procedures as follows; 1. preprocess of input dataset, 2. data exploration, 3. variable selection, 4. training of a model, and 5. Validation of the model. We added PI variables in the steps (i) in-between 2 and 3 steps (called PI-VM_{STA}) and (ii) in-between 3 and 4 steps (called VM_{STA}+PI). Each VM model are developed and evaluated by using 50 sets of SiO_2 etching depth data, having 20:1 aspect ratio and less than 5 % of variation. PI_{EEDF}, representing variation of electron energy distribution function (EEDF) is obtained from analysis of OES, which is based on the argon excitation kinetics. Pearson's correlation filter, principal component analysis (PCA), and stepwise variable selection are used for the variable selection methods. Results show that VM models using PI_{EEDF} have better performance than any other conventional VM models because PI_{EEDF} has much higher correlation with output variable than the other equipment and sensor variables. Especially, PI-VM_{STA} using stepwise variable selection method shows the highest accuracy where PI_{EEDF} provides a basis to select other OES variables. This study shows that a phenomenological-based, statistically tuned VM can be developed by using PI variables as input. It has advantages for management of dataset and selection of control variables in APC application.

5:40pm **PS-ThA11 Model Predictive Control of Plasma Density in Ar/SF_6 Capacitively Coupled Plasma Source***, **Sangwon Ryu**, H.-J. Roh, Y. Jang, D. Park, J. Koo, J.M. Lee, G.-H. Kim,* Seoul National University, Republic of Korea

Advanced Process Control (APC) of plasma assisted processes has drawn interests because the reproducibility of process results is degraded by continuous deterioration of the equipment. To control the process drift, the process plasma should be maintained by in-situ controller. Some earlier researches handled real-time feedback proportional integral derivative (PID) controllers for plasma density which is coupled to generation of the reactive species in plasma assisted processes. However, since PID had no knowledge of the controlled system, PID couldn't guarantee optimal control especially for systems with long dead time. Thus, we proposed model predictive controllers (MPC) for plasma density in Ar/SF_6 etching plasma as the control model of the MPC contains information of the system. To provide plasma density to the controller in real-time, we developed plasma density monitoring module which used light emissions from Ar measured by a spectrometer. The method showed $R^2 = 0.99$ with plasma density measured by Langmuir probe. The control model of the MPC was set as First Order Plus Dead Time (FOPDT) model which consisted of the linear gain and the time constants. We trained the control model with sensitivity tests; observing variation of plasma density as changing RF power. Compared to PID, MPC showed 6 times shorter settling time in set point tracking tests. Also, the integral of the absolute error for the MPC was 4 times lower than that of PID in same tests. The experimental results showed that MPC could control plasma more effectively than PID could by predicting the dead time of the system included in the control model. From the analysis on the parameters of the control model, we explained the control model as function of system parameters; the linear gain represented the balance between the power absorbed by electron and the power lost by electron impact collisions and the time constants were composed of the data transfer time between devices and the actuation time of the devices. This study showed that MPC could be used as the etching process plasma controller which would be a part of APC.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 202A - Session SA+AS+HC+SS-ThA

IoT Session: Multi-modal Characterization of Energy Materials & Device Processing

Moderators: Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy, Slavomir Nemsak, Advanced Light Source, Lawrence Berkeley National Laboratory

2:20pm **SA+AS+HC+SS-ThA1 Revealing Structure-Function Correlations in Fuel-Cells and Batteries.***, **Klaus Attenkofer**, E. Stavitski, M. Liu, D. Lu, M. Topsakal, D.J. Stacchiola, M.S. Hybertsen,* Brookhaven National Laboratory **INVITED**

To reveal the structure and even more important, the structure-function correlation of materials are essential prerequisites to the optimization and rational design of materials in energy storage and conversion applications. The complex processes resulting in the function typically involve not only the initial chemical reaction but a wide range of reorganizations, phase transitions, and transport phenomena which finally determine the efficiency of the material and its reliability in applications. The characterization challenge of visualizing changes on multiple length scales of ordered and disordered materials is one aspect of the characterization problem; to correlate the identified changes with the function of the material and distinguish the essential changes from other non-correlated alternation is the second equally important task.

In the talk we will show on various examples from the field of fuel cells and batteries, how high throughput hard X-ray spectroscopy can be combined with data analytics and theory to reveal the atomic structure of the ordered and disordered materials. In a next step a true imaging tool like transmission electron microscopy is used to verify this structure. The high throughput aspect of this approach provides not only a new opportunity to use database approaches to guarantee an unbiased method for the structure identification and optimization with a "field of view" in the nanometer range but also provides a new strategy to use data analytics, especially data mining approaches, to establish the structure-function correlation. The combination of ex-situ and operando experiments provides a statistical relevant data quantity and a diversity of the data necessary to this approach and is minimizing at the same time challenges caused by sample damage.

3:00pm **SA+AS+HC+SS-ThA3 Soft X-ray Spectroscopy for High Pressure Liquid***, **Ruimin Qiao**, J.-H. Guo, W. Chao,* Lawrence Berkeley National Laboratory **INVITED**

Soft X-ray spectroscopy (~50-1500eV), including both X-ray absorption and emission, is a powerful tool to study the electronic structure of various energy materials. Its energy range covers the K-edge of low-Z elements (e.g. C, N, O and F) and the L-edge of transition metal. Important information such as chemical valence, charge transfer and different ligand field could be directly extracted from the spectra. However, its application has been largely limited in materials that could be placed in vacuum (such as solid, below-ambient-pressure gas and liquid) because of the short penetration depth of soft x-ray. In this presentation, I will talk about the recent development of soft x-ray spectroscopy for high pressure liquid(up to 400 bars) at Advanced Light Source in Lawrence Berkeley National Lab.

4:00pm **SA+AS+HC+SS-ThA6 Surface Action Spectroscopy Using FHI FEL Infrared Radiation***, **Zongfang Wu**, H. Kuhlenbeck, W. Schöllkopf, H.J. Freund,* Fritz-Haber Institute of the Max Planck Society, Germany

In model catalysis and general surface science studies, the vibrational characterization of a surface is usually performed with HREELS (high-resolution electron energy loss spectroscopy) or IRAS (infrared reflection absorption spectroscopy). Both methods have disadvantages: HREELS suffers from its low resolution and (in the case of ionic samples) the presence of intense multiple phonon losses, while IRAS requires normalization of the spectrum with the spectrum of a reference sample, which leads to a contamination of the spectrum with features of the reference sample. Action spectroscopy with rare-gas messenger atoms [A. Fielicke et al., Phys. Rev. Lett. 93, 023401 (2004)] is an established method for vibrational spectroscopy of gas-phase clusters that avoids these disadvantages. Rare-gas atoms attached to gas-phase clusters may desorb when the incident infrared (IR) radiation is in resonance with a cluster vibration. The fragmentation rate, as monitored with a mass spectrometer, represents a vibrational spectrum, which can be used to draw conclusions regarding the cluster structure. Clusters, in this case deposited on a surface, are also highly relevant in model catalysis since they greatly influence catalytic reaction paths of supported catalysts. Both cluster shape and size matter. With this topic in mind a new apparatus for the application of IR FEL radiation to action spectroscopy of solid surfaces was set up at the Fritz Haber Institute (FHI), the V_2O_3(0001)/Au(111) (~10 nm thick) and a TiO_2(110) single crystal surface were studied as first test systems. The machine is connected to the FHI FEL, which is able to provide intense and widely tunable (3 – 60 µm) IR radiation. For V_2O_3(0001)/Au(111) the well-characterized vanadyl surface vibration and other surface vibrations could be detected, while bulk states turned out to be invisible to the method. Presumably, anharmonic vibrational coupling between the primary excited vibration and the rare-gas vs. surface vibration leads to desorption. This explains the surface sensitivity of the method as well as its insensitivity to bulk vibrations. In the case of the TiO_2(110) single crystal also rare-gas desorption resulting from an IR induced increase of the crystal temperature could be observed. This led to a better understanding of polaritons in rutile.

4:20pm **SA+AS+HC+SS-ThA7 Spectroscopic Insight into Resistive Switching Processes in Oxides***, C. Baeumer, C. Schmitz,* Forschungszentrum Juelich GmbH, Germany*; A. Kindsmüller,* RWTH Aachen University, Germany*; N. Raab, V. Feyer, D.N. Mueller, J. Hackl, S. Nemsak,* Forschungszentrum Juelich GmbH, Germany*; O.T. Mentes, A. Locatelli,* Elettra-Sincrotrone Trieste, Italy*; R. Waser, R. Dittmann,* ***Claus Michael Schneider,*** Forschungszentrum Juelich GmbH, Germany

Nonvolatile memories play an increasing role in modern nanoelectronics. Among the various storage concepts, resistive switching promises a high scalability. In oxides, the physical mechanism behind resistive switching involves electrically controlled local redox processes, which result in the formation and migration of oxygen vacancies. We studied these redox processes and their influence on the resistive switching in the model systems $SrTiO_3$(STO) and $ZrO_2$with a full suite of synchrotron-radiation based spectroscopy techniques. The resistive switching in STO proceeds via the growth of nanoscale conductive filaments, which poses considerable challenges to the spectroscopic characterization. Employing nanospectroscopy in an *operando* configuration we could unanimously relate the conductivity changes between the ON (low resistance) and OFF states (high resistance) to the redox-induced changes of the valencies and the formation of oxygen vacancies [1,2]. The retention time of the ON state in STO is determined by a reoxidation of the previously oxygen-deficient region and can be controlled by inserting an oxygen diffusion barrier. With respect to the reproducibility of the switching process, we find that the individual switching event is governed by a competition within a network of subfilaments, which has been created in the initial forming step. Upon resistive switching, one of these subfilaments becomes the current-carrying filament. However, during repeated switching the different subfilaments may become active, resulting in a cycle-to-cycle variation of the location and shape of the current-carrying filament, which determines the low-resistance state [3].

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[2] A. Kindsmüller, C. Schmitz, C. Wiemann, K. Skaja, D. J. Wouters, R. Waser, C. M. Schneider and R. Dittmann, APL Materials **6** (2018) 046106.

[3] C. Baeumer, R. Valenta, C. Schmitz, A. Locatelli, T. O. Mentes, S. P. Rogers, A. Sala, N. Raab, S. Nemsak, M. Shim, C. M. Schneider, S. Menzel, R. Waser and R. Dittmann, ACS Nano **11** (2017) 692.

4:40pm **SA+AS+HC+SS-ThA8 Visualizing Electronic Structures of Topological Quantum Materials by Synchrotron Based Photoemission Spectroscopy***,* ***Yulin Chen,*** Oxford University, UK **INVITED**

The electronic structure of matter is critical information that determine its electric, magnetic and optical properties. The precise understanding of such information will not only help understand the rich properties and physical phenomena of quantum materials, but also guide the design of their potential applications.

Angle-resolved photoemission spectroscopy (ARPES) is an effective method in determining the electronic structures of materials: with its energy and momentum resolution, ARPES can directly map out dispersions of electronic bands in the reciprocal space with critical parameters (such as the energy gap and width of bands, carrier type, density and the Fermi-velocity, etc.).

In this talk, I will first give a brief introduction to this powerful experimental technique, its basic principle and the rich information it can yield by using synchrotron radiation light source, then focus on its recent application to topological quantum materials (including some of our works on topological insulators, Dirac and Weyl semimetals [1]). Finally, I will review the recent development in ARPES and give a perspective on its future directions and applications.

[1] Science, 325, 178 (2009), Science, 329, 659 (2010), Nature Nanotechnology, 6, 705 (2011), Nature Chemistry, 4, 281 (2012), Nature Physics, 9, 704 (2013), Science, 343, 864 (2014), Nature Materials, 13, 677 (2014), Nature Physics, 11, 728 (2015), Nature Materials, 15, 27(2016), Nature Communications 7, 12924 (2016), Nature Communications, 8, 13973 (2017).

5:20pm **SA+AS+HC+SS-ThA10 Electronic Structure of FeO, γ-Fe_2O_3 and Fe_3O_4 Epitaxial Films using High-energy Spectroscopies***,* ***German Rafael Castro,*** Spanich CRG BM25-SpLine Beamline at the ESRF,, France*; J. Rubio Zuazo,* Spanish CRG BM25-SpLine at the ESRF, France*; A. Chainani,* Condensed Matter Physics Group, NSRRC, Taiwan, Republic of China*; M. Taguchi,* RIKEN SPring-8 centre, Japan*; D. Malterre,* Institut Jean Lamour, Universite de Lorraine, France*; A. Serrano Rubio,* Spanich CRG BM25-SpLine Beamline at the ESRF, France

Today, one of the materials science goals is the production of novel materials with specific and controlled properties. Material composites, which combine different materials, with specific and defined properties, mostly of multilayer thin films, are a promising way to create products with specific properties, and, in general different of those of the constituents. The chemical, mechanical, electric and magnetic properties of such materials are often intimately related to their structure, composition profile and morphology. Thus, it is crucial to yield with an experimental set-up capable to investigate different aspects related with the electronic and geometric structure under identical experimental conditions, and, in particular, to differentiate between surface and bulk properties. There are few techniques able to provide an accurate insight of what is happening at these interfaces, which in general are buried by several tens of nanometres inside the material. The Spline beamline Branch B at the ESRF, the European Synchrotron, offers unique capabilities in this respect.

In this contribution we will present the study of the electronic structure of well-characterized epitaxial films of FeO (wustite), γ-Fe_2O_3 (maghemite) and Fe_3O_4 (magnetite) using Hard X-ray Photoelectron Spectroscopy (HAXPES), X-ray Absorption Near Edge spectroscopy (XANES) and electron energy loss spectroscopy (EELS). We carry out HAXPES with incident photon energies of 12 and 15 keV in order to probe the bulk-sensitive Fe 1s and Fe 2p core level spectra. Fe K-edge XANES is used to characterize and confirm the Fe valence states of FeO, γ-Fe_2O_3 and Fe_3O_4 films. EELS is used to identify the bulk plasmon loss features. A comparison of the HAXPES results with model calculations for an MO6 cluster provides us with microscopic electronic structure parameters such as the on-site Coulomb energy U_{dd}, the charge-transfer energy Δ, and the metal-ligand hybridization strength V. The results also provide estimates for the ground state and final state contributions in terms of the d^n, d^{n+1}L1 and d^{n+2}L2 configurations. Both FeO and γ-Fe2O3 can be described as charge-transfer insulators in the Zaanen-Sawatzky-Allen picture with $U_{dd} > \Delta$, consistent with earlier works. However, the MO6 cluster calculations do not reproduce an extra satellite observed in Fe 1s spectra of γ-Fe_2O_3 and Fe_3O_4. Based on simplified calculations using an M2O7 cluster with renormalized parameters, it is suggested that non-local screening plays an important role in explaining the two satellites observed in the Fe 1s core level HAXPES spectra of γ-Fe_2O_3 and Fe_3O_4.

5:40pm **SA+AS+HC+SS-ThA11 Single-Bunch Imaging of Detonation Fronts Using Scattered Synchrotron Radiation***, M.H. Nielsen, J.A. Hammons, M. Bagge-Hansen, L.M. Lauderbach, R. Hodgin, K. Champley, W. Shaw,* Lawrence Livermore National Laboratory*; N. Sinclair,* Washington State University*;* ***Trevor Willey,*** Lawrence Livermore National Laboratory

Radiographic imaging using a series of single pulses from synchrotron storage rings or x-ray free-electron lasers gives new insight into dynamic phenomena. One limitation of these sources is that the native and natural beam size at most end-station hutches is, at best, of mm-scale dimensions. Here, we describe a method for collecting full-field, radiographic images of cm-scale phenomena using focused pink-beam and scattering the x-rays, effectively creating point-source images. Although currently photon starved and highly dependent on parameters chosen (such as source-to-object and source-to-detector distances, scattering material, etc.) we are continuously improving the technique. At the Dynamic Compression Sector at the Advanced Photon Source, we use this capability to image detonation phenomena, particularly direct imaging of detonator performance, imaging initiation and run-up to detonation, imaging differences in ideal vs. non-ideal explosives, and have a goal to determining density during detonation at 10's of microns in resolution. In this presentation, we summarize our progress developing and using this technique in creating movies of dynamic phenomena as fast as 153.4 ns between frames, and as a method for imaging samples prior to, for example, collecting dynamic small-angle x-ray scattering or diffraction to observe nanodiamond growth kinetics and composition evolution during detonation.

Surface Science Division
Room 203C - Session SS+AS+BI+MI+NS-ThA
Organic/Inorganic Surfaces, Interfaces and Nanostructures

Moderator: Denis Potapenko, Princeton University

2:20pm **SS+AS+BI+MI+NS-ThA1 Investigation of the Stability of Ag Monolayers on Au(111) as a Function of Metal Adatom Diffusion***, J.A. Phillips, L.K. Harville, H.R. Morgan, L.E. Jackson, G. LeBlanc,* ***Erin Iski****,* University of Tulsa

The formation of an atomically thin, Ag layer on a Au(111) surface has been shown to significantly alter the thermal properties of the underlying substrate (1). A further exploration into the chemical mechanisms by which these thin films are deposited reveals two different sources of Ag during the formation of the monolayer. Electrochemical Scanning Tunneling Microscopy (EC-STM) and Cyclic Voltammetry (CV) are used to probe the *in-situ* interfaces of these metal systems as well as the adsorption of molecules on metals. EC-STM is a unique technique that, in addition to providing a local probe of the atomic surface structure, also functions as a 3-electrode cell in which redox chemistry can be performed to understand the chemical reactivity of the surface. Also, cyclic voltammograms (CVs) can be generated to provide specific information regarding the nature of the redox events occurring at the surface. The two sources of silver used for the Underpotential Deposition (UPD) process on Au(111) result in significantly different thermal stabilities of the surface. An important question is whether this stability can extend beyond thermal properties, which will be probed using the assembly of amino acids on Ag/Au(111). Using both EC-STM and UHV-STM (ultra-high vacuum STM), it has been shown that amino acids assist in the immobilization of diffusing adatoms on the surface and in the subsequent formation of metal islands (2). Since the molecular deposition in both cases takes place at room temperature, the current understanding is that the atoms on the surface are a function of the temperature of the surface and are not pulled out of the surface itself. Importantly, these systems provide a unique glimpse into metal surface diffusion and offer the ability to study the mass transport of metal atoms. This study focuses on how an application of the thin Ag film on the Au(111) will disrupt or assist in the metal adatom transport and whether the known thermal stability can extend to other surface properties, thus making the afforded stability more general. The interaction of the amino acids with the Ag films deposited at the two different potentials and the associated mass transport as measured by the size of metal islands on the surface will shed light on the stabilities of the two types of Ag layers. The ability to experimentally choose different surface properties based on electrochemical parameters and solution composition during metal deposition could lead to exciting new directions for thin film technologies.

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

(2) Iski *et al. submitted to Communication Chemistry, May 2018.*

2:40pm **SS+AS+BI+MI+NS-ThA2 Chain-Length Dependent Reactivity of Thiolate Self-Assembled Monolayers with Atomic Gas Species***,* ***Jeffrey Sayler****, S. Brown, S.J. Sibener,* University of Chicago

Thiolate self-assembled monolayers (SAMs) provide platforms for easily customizable organic interfaces, making them an excellent model system for studying the chemical properties of organic thin films. In particular, their reactions with atomic gas species such as hydrogen and oxygen yield important information about gas-surface interactions in organic films, how static and dynamic disorder influence passivation, as well as various hydrogenation and oxidation reactions. We are currently investigating the reactions of these SAMs with atomic hydrogen (H), using an angle-directed atomic gas source and *in situ* ultra-high vacuum scanning tunneling microscopy (UHV-STM). First, a series of alkanethiolate SAM samples of varying chain length (8 to 11 carbon atoms long) were reacted with H, resulting in the monolayers' conversion from close-packed standing-up phase to lower density lying-down phase. Regardless of chain length or even-/oddness, which were expected to impact the effectiveness of H penetration into the monolayer due to differences in the chains' lateral mobility and terminal structure, all samples exhibited common kinetic mechanistic details. The relative reaction rates of different chain lengths were obtained using simultaneous dosing of multiple samples. Second, a close-packed 1H,1H,2H,2H-perfluorodecanethiol SAM (a fluorinated analog of the 1-decanethiol SAM) was reacted with H. Dosing this sample under the same conditions as the 1-decanethiol sample revealed little to no reactivity. Ongoing studies continue to explore the reactivity of this family of saturated SAM systems including investigation of the kinetics and mechanism of the lying-down phase's reactivity with H. Further investigations involving atomic oxygen and different SAM chemical compositions and structures will follow.

3:00pm **SS+AS+BI+MI+NS-ThA3 Scan Probe Studies of Lithium Transfer through Solid State Electrochemical Interfaces***,* ***Janice Reutt-Robey****,* University of Maryland College Park **INVITED**

All solid-state electrical energy storage devices are of immense interest as safer alternatives to those based upon flammable liquid electrolytes. Understanding the rates and elementary processes for lithium ion transport through anode-solid electrolyte-cathode interfaces is essential, but obscured by heterogeneous samples and unknown local potentials. I will present new nanoscale studies of lithiation/delithiation across well-defined interfaces created with actuated nanobattery junctions. Conventional STM metallic tips, clad with a thin film of electrode material ($LiCoO_2$ or Li) and a capping film of solid electrolyte ($Li_xAl_2O_3$ or Li_20), function as ½ cells. Probes are positioned and electrochemically cycled at singular surfaces of model electrodes – Si(111), Si(100), C(0001). At the nanoscale, hysteresis in charging/discharging is monitored as a function of interface structure and materials properties. UHV measurements preserve the chemical integrity of the material interfaces and allow traditional (cyclic voltammetry, stepped potential) and nontraditional (stepped stress) electrochemical measurements to separate electron/ion contributions to charge transfer. The data reveal how induced variations in local lithium concentration impact rates for charging/discharging and contribute to hysteretic behavior. Further, stress-induced current transients show non-Cotrellian time behavior, attributed to a lithium ion concentration gradient in the solid electrolyte. Modeling of nanobattery data allows for testable predictions of material properties. Finally we show how "inverted" Scanning Tunneling Spectroscopy provides a useful tool to characterize the electrical band gap of the tip 1/2 cell materials, while imaging reveals the distribution pattern of lithium ions at the cycled electrode surfaces.

This work was supported as part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award number DESC0001160.

4:00pm **SS+AS+BI+MI+NS-ThA6 Adsorption and Self-assembly of Halogenated Organic Molecules on the Si(111) √3×√3-Ag Surface***,* ***Renjie Liu****,* Lakehead University, Canada*; C. Fu, A.G. Moisseev, M.R. Rao, Y. Chen, D.F. Perepichka,* McGill University, Canada*; M.C. Gallagher,* Lakehead University, Canada

Given potential applications in molecular electronics, organic thin films continue to attract a great deal of scientific attention. Furthermore, organic-inorganic semiconductor hybrids have been identified as a possible platform for future devices. Generally such a device would require thin films of functionalized organic molecules grown on silicon surfaces. To promote the growth of high quality films, the Si surface needs to be passivated. For example, the Si(111) √3×√3-Ag surface has been shown to be weakly interacting, allowing molecules to remain mobile and form well ordered layers [1].

In this work we compare the adsorption and self-assembly of two halogenated molecules of threefold symmetry; 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (TIPT), and tribromotrioxaazatriangulene (TBTANG) on the Si(111)-√3×√3-Ag surface. The self assembly of TIPT on HOPG and Au(111) has been reported previously [2], and heteroatom forms of triangulene are of particular interest in molecular electronics [3].

We find that both molecules display high mobility on the √3-Ag surface. With increasing molecular dose, TIPT forms supramolecular domains defined by a 2.0 nm by 1.8 nm rectangular cell. The size and symmetry of the unit cell provides strong evidence that a large fraction of the monomers do not undergo de-halogenation, and that the dominant interaction within the domains is intermolecular I···H hydrogen-bonding. As the coverage approaches one monolayer, the film consists of supramolecular domains of limited extent separated by regions of disorder. STM images at lower coverage reveal that molecular adsorption increases the defect density of the underlying $\sqrt{3}$-Ag layer. We believe that a small fraction of the TIPT molecules de-iodinate on adsorption and that the iodine subsequently reacts with the Ag overlayer. The increased defect density limits the extent of the supramolecular domains on this surface.

In contrast, TBTANG exhibits long-range self-assembly of intact molecules. The ordered structure is characterized by several closely packed rows of molecules. Within the rows the repeating motif is two-molecules linked together by Br···Br interactions. With increasing coverage, the $\sqrt{3}$ surface remains unaffected and the self assembled layer extends over the entire surface.

[1] Yokoyama, T. *et al.*, *J Chem Phys* **142**, 204701 (2015).

[2] Gatti, R. *et al.*, *J. Phys. Chem. C* **118**, 25505–25516 (2014).

[3] Nakatsuka, S. *et al.*, *Angewandte Chemie* **129**, 5169–5172 (2017).

4:20pm **SS+AS+BI+MI+NS-ThA7 Electron Interactions with Alkanethiol Self-assembled Monolayers on Au(111)***, **Jodi Grzeskowiak**,* University at Albany-SUNY*; C.A. Ventrice, Jr.,* SUNY Polytechnic Institute

Self-assembled monolayers (SAMs) are often used for applications such as molecular electronics, selective deposition, and various forms of surface modification. Advanced lithography within the semiconductor industry is adopting ever shorter wavelengths of light such that the interaction of secondary electrons with the organic resist is becoming the primary mechanism for photo-initiated electro-chemical solubility changing reactions. In order to study the interaction of low energy electrons with thin organic films, measurements have been performed on electron decomposition of alkanethiol molecules grown on Au(111) substrates. SAMs have been grown via both solution and vapor phase methods. These monolayers arrange into two distinct phases commonly referred to as lying down and standing up. The lying down phase is a physisorbed layer that is only weakly interacting with the substrate via Van der Waals forces. Conversely, the standing up phase is a chemisorbed species that is more strongly bound to the substrate. Various surface analysis techniques were used to characterize the monolayers before and after electron exposure. Low energy electron diffraction (LEED) was used to determine the structure of the SAM and the rate of decomposition. Temperature programmed desorption (TPD) in combination with mass spectrometry was used to evaluate the thermal stability and bonding strength of the attached SAMs and the decomposition products from electron exposure.

4:40pm **SS+AS+BI+MI+NS-ThA8 Measuring the Electronic Properties of Organic Single Crystals***, **Sujitra Pookpanratana**, E.G. Bittle, C.A. Hacker, S.W. Robey,* National Institute of Standards and Technology (NIST)*; R. Ovsyannikov, E. Giangrisostomi,* Helmholtz-Zentrum Berlin, Germany

Organic and molecular-based compounds have found commercial application in consumer-based electronics. Organic semiconductors can be integrated onto device structures in different physical forms such as single crystals, polycrystalline thin-films, or amorphous thin-films. The structural order of the molecular solid profoundly influences the electronic properties, that in turn controls important properties, such as the transport gap and binding energy of the highest occupied molecular orbital (HOMO) [1, 2], that govern how an electronic device operates. Photoemission can play a vital role in illuminating these important electronic properties. While there are numerous photoemission spectroscopic measurements of organic semiconductors in thin-film structures, far fewer attempts have been made to determine the "fundamental" electronic properties for pristine organic single crystals.

Here, we present results of photoemission measurements for single crystalline (SC) dinaphthothienothiophene (DNTT). DNTT is a small molecule-based thienoacene and has demonstrated carrier mobilities approaching $10\ cm^2/(V\ s)$ [3], is air-stable [4] and durable against accelerated temperatures and humidity conditions.[5] While there are many device studies that establish DNTT and other related thienoacenes for a variety of applications, detailed electronic and chemical structure studies are lacking. Electronic "band" structure measurements using a novel angle-resolved time-of-flight electron spectrometer is performed on SC-DNTT, and multiple highest occupied molecular orbitals are resolved of varying widths. Modest dispersion of the frontier HOMO is observed, and this result will be discussed in context of the charge carrier behavior of DNTT reported in the literature.

[1] J. Ivanco et al., Adv. Mater. 15, 1812 (2003)

[2] S. Krause et al., Org. Electron. 14, 584 (2013)

[3] W. Xie et al., Adv. Mater. 25, 3478 (2013)

[4] U. Zschieschang et al., Adv. Mater. 22, 982 (2010)

[5] N. K. Za'aba et al., Org. Electron. 45, 174 (2017)

5:00pm **SS+AS+BI+MI+NS-ThA9 Surface Functionalization of Porous Substrates via Initiated Chemical Vapor Deposition***, **Christine Cheng**, M. Gupta,* University of Southern California

Porous materials are used in various applications including separation membranes, paper-based microfluidics, and flexible electronics. Tuning surface properties of porous materials enhances the versatility of existing materials, giving them new functions and applications. However, traditional surface modification methods are typically solvent-based, which limits the range of substrates that can be coated. In this work, initiated chemical vapor deposition was used to continuously modify the surface of large areas of porous substrates in an all-dry vacuum process. A superhydrophobic polymer was deposited onto a porous substrate and the coating was characterized using contact angle goniometry, X-ray photoelectron spectroscopy, and scanning electron microscopy to study the uniformity of the coating along the entirety of the substrate. The superhyodrophobicty of the coated porous substrate is attributed to the deposited polymer and the roughness of the substrate. Addition of a perfluorinated liquid to the superhydrophobic porous substrate formed a slippery liquid-infused porous surface. A hydrophilic polymer was deposited on top of the superhydrophobic polymer to demonstrate the facile stacking of polymer layers with different chemistries using this process.

5:20pm **SS+AS+BI+MI+NS-ThA10 Atomic-Scale Understanding of Anatase Nanocatalyst Activation***, **William DeBenedetti**[1], E.S. Skibinski, M.A. Hines,* Cornell University

Our ability to predict the chemical reactivity of nanocatalysts has been stymied by our lack of atomic-scale understanding of nanocatalyst surface structure. Specifically, do nanocatalyst surfaces adopt a bulk-terminated structure or do they reconstruct to minimize their surface free energy, thereby lowering their chemical reactivity as observed in ultra-high vacuum? Furthermore, do nanocatalysts processed at higher temperature maintain their low-chemical-reactivity, reconstructed surfaces when used at low temperatures and under typical operating conditions?

Using a new technique for the growth of highly aligned anatase (001) nanocatalysts, we will show that solution-synthesized anatase is terminated by a monolayer of fluorine, which acts as an atomic-scale protective coating against adventitious contamination. We will also show that carboxylic acid solutions, the most common TiO_2 functionalization chemistry, causes a spontaneous reorganization of a reconstructed nanocatalyst, leading to a five-fold increase in the number of reactive sites. This surface reorganization is not observed when carboxylic acids are dosed from the gas phase, indicating that experiments in ultra-high vacuum environments lead to trapped states that may not be relevant to nanocatalysts in ambient conditions. *Ab initio* calculations show that although the carboxylic acid termination is slightly less effective at removing surface stress than the reconstructed surface, it is more effective in lowering the surface free energy. These findings suggest that bulk-terminated metal oxide nanocatalysts may be common under ambient operating environments, even after high-temperature processing or if reactants are rinsed off.

5:40pm **SS+AS+BI+MI+NS-ThA11 Mechanistic view of Solid-Electrolyte Interphase Layer Evolution at Li-metal Anode***, **Venkateshkumar Prabhakaran**,* Physical Sciences Division, Pacific Northwest National Laboratory*; M.H. Engelhard, A. Martinez,* Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory*; G.E. Johnson,* Physical Sciences Division, Pacific Northwest National Laboratory*; S. Thevuthasan,* Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory*; V. Murugesan,* Physical Sciences Division, Pacific Northwest National Laboratory

A molecular-level understanding of structural and chemical transformations of electrolyte at solid-electrolyte interfaces (SEI) is critical for rational design of electrochemical materials. Despite numerous studies,

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[1] **National Student Award Finalist**

evolution of the transient and metastable species which dictates the cascade of interfacial reactions are still not clear. The challenge is to establish the chemical homogeneity within interface to clearly delineate the origin of various decomposition reaction products and their energetic pathways. Soft landing of mass-selected ions is ideally suited for building the interface with selected constituent which can alleviate the complexity associated with diverse and correlated processes within SEI layer.[1-4] Herein, we report the development and first demonstration of new capabilities that combine ion soft landing with *operando* infrared reflection-absorption spectroscopy (IRRAS) to study the decomposition of counter anions and solvent molecules on bare lithium metal surfaces. Specifically, we discreetly deposited sulfonyl imide based electrolyte anion ($TFSI^-$) and solvated Lithium cations without corresponding counter ions onto bare lithium metal using soft landing approach and monitored their decomposition using *in-situ* IRRAS and *ex-situ* x-ray photoelectron spectroscopy (XPS). *Operando* IRRAS and XPS measurements captured the signatures of transient species arising from decomposition of electrolyte anions and solvent molecules in real time. We will discuss, our unique approach of building interface with precise control over the constituents and subsequently detect the spectroscopic signatures of transient species during decomposition processes.

References:

1. Johnson, G. E.; Hu, Q.; Laskin, J., Soft landing of complex molecules on surfaces. *Annual Review of Analytical Chemistry* **2011,***4*, 83-104.
2. Prabhakaran, V.; Mehdi, B. L.; Ditto, J. J.; Engelhard, M. H.; Wang, B.; Gunaratne, K. D. D.; Johnson, D. C.; Browning, N. D.; Johnson, G. E.; Laskin, J., Rational design of efficient electrode–electrolyte interfaces for solid-state energy storage using ion soft landing. *Nature Communications***2016,***7*, 11399.
3. Prabhakaran, V.; Johnson, G. E.; Wang, B.; Laskin, J., *In situ* solid-state electrochemistry of mass-selected ions at well-defined electrode–electrolyte interfaces. *Proceedings of the National Academy of Sciences* **2016,***113*, 13324-13329.
4. Gunaratne, K. D. D.; Johnson, G. E.; Andersen, A.; Du, D.; Zhang, W.; Prabhakaran, V.; Lin, Y.; Laskin, J., Controlling the Charge State and Redox Properties of Supported Polyoxometalates via Soft Landing of Mass-Selected Ions. *Journal of Physical Chemistry C* **2014,***118*, 27611-27622.

Surface Science Division
Room 102A - Session SS+EM+PS+TF-ThA

Deposition, Etching and Growth at Surfaces

Moderator: Bruce E. Koel, Princeton University

2:20pm **SS+EM+PS+TF-ThA1 Controlled Deposition and High-Resolution Analysis of Functional Macromolecules in Ultrahigh Vacuum***, Giovanni Costantini,* University of Warwick, UK **INVITED**

The ultimate spatial resolution of scanning tunnelling microscopy (STM) has allowed to gain an exceptional insight into the structure and the intra- and inter-molecular bonding of a huge number of adsorbed molecular system. Unfortunately, these remarkable analytical capabilities are achieved only under ultrahigh vacuum (UHV) conditions and therefore cannot be directly applied to more interesting systems composed of functional (bio)molecules or complex synthetic compounds. In fact, thermal sublimation is the strategy of choice for preparing ultrathin films of small and heat-resistant molecules in UHV but larger, complex (bio)molecules are not compatible with this process.

This challenge has been overcome in recent years by adapting soft-ionisation techniques developed in mass spectrometry (mainly electrospray ionisation, ESI) to transfer intact fragile molecules into the gas phase and to soft-land them onto atomically flat and clean substrates. When combined with advanced scanning probe microscopes operating under UHV conditions, these novel set-ups allow the surface deposition and high-resolution characterisation of a wide range of functional organic molecules and inorganic nanoparticles.

This talk will present recent advances in the development of ESI-deposition techniques and their combination with UHV-STM to analyse complex (bio)molecule-surface systems. It will start by reviewing the limits that standard molecular deposition imposes on the size of (bio)molecules that can by studied in surface science. It will continue by presenting a recently developed ESI-deposition setup based on a simple, efficient and modular design with a high intensity and mass selectivity. The discussion will then proceed to the application of ESI-STM to the characterisation of adsorbed polypeptides and polymers. In particular, it will be shown that this technique allows the imaging of individual macromolecules with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

3:00pm **SS+EM+PS+TF-ThA3 Unconventional Nucleation and Growth Kinetics: *in situ* Variable-temperature Scanning Tunneling Microscopy Studies of Chemical Vapor Deposition of Inorganic Monolayers on Metallic Substrates***, **Pedro Arias,*** University of California, Los Angeles*; A. Abdulslam,* Colorado School of Mines*; A. Ebnonnasir,* University of California at Los Angeles*; C.V. Ciobanu,* Colorado School of Mines*; S. Kodambaka,* University of California, Los Angeles

The growth of thin films from atoms and/or molecules deposited from the gas phase onto solid substrates is a non-equilibrium phenomenon where the structure, composition, and crystallinity of the films are determined by kinetic and thermodynamic processes. Over the past few decades, vast and fruitful efforts have been devoted to understanding the kinetics of thin film growth. As a result, conventions of the kinetic factors have been developed to predict the growth mechanism and, hence, microstructure of the as-grown films: for example, nucleation at terraces (steps) is expected to occur when surface diffusion of adsorbed species is significantly lower (higher) compared to the deposition flux and is observed at higher (lower) fluxes and lower (higher) substrate temperatures. Here, we report an unconventional growth mode of inorganic monolayers on metallic substrates.

Using in situ ultra-high vacuum scanning tunneling microscopy (UHV STM), we investigated the chemical vapor deposition (CVD) kinetics of hexagonal boron nitride (hBN) monolayers on Pd(111). In each experiment, STM images are acquired while exposing Pd(111) to borazine (10^{-7} – 10^{-6} Torr) at temperatures 573 K and 673 K and for times up to 2500 s. The STM images reveal the nucleation and growth of two-dimensional islands on the Pd surfaces. From the images, we measure the areal coverage, island sizes, and island density as a function of time, temperature, and borazine flux. We find that the rates of areal coverage and island density increase ten-fold with increasing borazine pressure from 10^{-7} to 10^{-6} Torr at 573 K and three-fold with increasing temperature from 573 K to 673 K and borazine pressure of 10^{-7} Torr. Our STM images reveal an unusual nucleation and growth mode: at lower deposition flux and higher temperature, islands form on terraces; increasing the flux and/or lowering the temperature result in preferential nucleation and growth at the step edges. Interestingly, the step-edge growth of borazine islands is observed on *both* up and down steps. We attribute this phenomenon to the structure and the highly anisotropic bonding of borazine on Pd(111). Our results provide new insights into the growth dynamics of two-dimensional layered materials.

3:20pm **SS+EM+PS+TF-ThA4 Redox-Active Ligands for Single-Site Metal-Organic Complexes on Surfaces as Heterogeneous Catalysts***, **Tobias Morris,*** Indiana University*; D.L. Wisman,* Indiana University, NAVSEA Crane*; I.J. Huerfano, N.A. Maciullis, K.G. Caulton, S.L. Tait,* Indiana University

The utilization of single-site transition metal centers at surfaces is of growing interest in the heterogenous catalysis community. One advantage of single-site metal centers is the high dispersion so that a much higher fraction of atoms contribute to chemical activity compared to nanoparticle catalysts. Our approach to forming single-site metal centers is on-surface complexation with a redox-active ligand, which allows a high degree of ordering on the surface as well as intimate chemical contact of the metal center with the support surface. The ligand design enables us to tailor the coordination geometry and oxidation state of the metal and thus affect the cooperation between metal and ligand and the chemical reactivity. Several ligands, differing in backbone, binding pocket, design, and peripheral units were examined in this study. Tetrazine-based ligands are known for their redox activity. The on-surface two-electron redox process utilizes vapor deposition of 3,6-di-2-pyridyl-1,2,4,5-tetrazine (DPTZ) with vanadium cations onto an Au(100) surface. The metal-organic complexation leads to the growth of 1D chains consistent of one metal per ligand due to the divergent binding pockets created by the tetrazine core and pyridine rings. Exposing the V-DPTZ chains to oxygen results in a dissociative reaction of molecular oxygen to form a terminal oxo species on the vanadium, while allowing the metal-organic complex to remain intact. Interestingly, the dioxygen activation contributes adsorbed oxygen to the support surface by a spillover mechanism. The stable V-oxo species is the only oxidation product, unlike the unselective oxidation of V nanoparticles. A newly synthesized ligand, tetraethyltetra-aza-anthraquinone (EtTAAQ), utilizes a quinone backbone with adjacent pyrazine rings to generate four symmetric binding pockets. Quinones are one of the oldest studied redox-active ligands. EtTAAQ has the capacity for up to a four-electron reduction, enabling the possibility for multiple metal sites per ligand. Continued work on redesigning ligands is showing promise in increasing the cooperativity of the ligand and the metal which could lead to heightened reactivity.

4:00pm **SS+EM+PS+TF-ThA6 Oxidation and Ablation of HOPG Using Supersonic Beams of Molecular Oxygen Combined with STM Visualization***, **Ross Edel**, T. Grabnic, B. Wiggins, S.J. Sibener,* University of Chicago

Graphite is widely studied due to its importance in high-performance materials applications such as high velocity flight systems as well as its key role as a model system for other carbonic materials such as graphene and carbon nanotubes. Our research focuses on the reaction of highly oriented pyrolytic graphite (HOPG) with molecular oxygen, the mechanism of which is not yet fully understood. Utilizing a one-of-a-kind instrument that combines a supersonic molecular beam and scanning tunneling microscope (STM) in ultra-high vacuum, we are able to tightly control the energy and angle of impinging oxygen and examine the nanoscopic and mesoscopic evolution of the surface. We have found that different oxygen energies, incident angles, and surface temperatures produce morphologically distinct etching features: Anisotropic channels, circular pits, and hexagonal pits faceted along crystallographic directions. The faceted and circular etch pits were formed at low O_2 energy, with faceting only apparent below a critical surface temperature, while anisotropic etching was observed with exposure to higher energy oxygen. Comparison of low- and high-grade reacted samples show that anisotropic channels likely result from the presence of grain boundaries. Reaction probability increased with beam energy and demonstrated non-Arrhenius behavior with respect to surface temperature, peaking at around 1375 K. Beam impingement angle had only minor effects on the reaction probability and etch pit morphology. Reactivity was enhanced by natural grain boundaries and artificially created point defects, showing the critical influence of small structural imperfections. Our combination of STM imaging with well-defined and controlled oxidation conditions connects interfacial reaction kinetics with time-evolving nanoscopic surface morphology, providing new insight into the oxidation of graphitic materials under high-temperature conditions. Spatio-temporal correlations obtained in this manner shed new light on interfacial erosion mechanisms, and provide an incisive complement to the information obtained using spatially-averaged gas-surface reactive scattering measurements.

5:00pm **SS+EM+PS+TF-ThA9 DLC Films by Modified HiPIMS with Effect from Pulse Parameters on Plasma Parameters and Film Quality***, **David Ruzic**, I. Haehnlein,* University of Illinois at Urbana-Champaign*; B. Wu,* Southwest Jiaotong University*; D. Barlaz,* University of Illinois at Urbana-Champaign*; B.E. Jurczyk,* Starfire Industries

Diamond like carbon (DLC) films have made waves as of late in many industries. DLC provides a high strength low friction surface with the potential for high chemical resistivity. High Power Impulse Magnetron Sputtering (HiPIMS) is a promising physical vapor deposition (PVD) that creates high ionization fractions at the substrate using high power pulses over low duty factors. The resulting high plasma densities (as high as 10^{19} m^{-3}) creates ionization fractions of sputtered material at the target surface. The increase in energy of atoms due to high ionization rates at the substrate yields higher density and smoother films. In combination with a positive polarity pulse to drive ions to the substrate surface, the DLC film hardness can be increased while producing a smoother film surface.

By introducing a larger ion flux, determined through a gridded energy analyzer, the ratio of sp^3 bonded carbon to sp^2 is presented for a multitude of parameters. This work explores not only the use of positive polarity pulses, but the effect of pulse parameters, has on film hardness and morphology. By controlling the deposition rate through pulse width and repetition rate while controlling deposition energy increases by approximately 5% in sp^3 fraction were observed while surface roughness decreased by a factor of 4 for a non-hydrogenated amorphous carbon film by just the introduction of a positive polarity pulse. Further increases are reported through fine tuning the discharge parameters while looking at plasma densities, ion fraction, surface roughness, sp^3 fraction, and hardness for DLC on silicon substrates.

5:20pm **SS+EM+PS+TF-ThA10 Adsorption and Reactions on Topological Insulators Surfaces Probed by Low Energy Ion Scattering***, **Haoshan Zhu**[1], W. Zhou, J.A. Yarmoff,* University of California - Riverside

Bi_2Se_3 and Bi_2Te_3 are two-dimensional topological insulators (TIs) that have attracted intense interest in recent years. TIs are promising candidates for superconductor, spintronics and quantum computing applications due to topological surface states (TSS) that connect the conduction and valence bands. The clean $Bi_2(Se,Te)_3$ surfaces prepared under ultra-high vacuum (UHV) are terminated with Se or Te, but the termination can change if exposed to air or prepared under non-ideal conditions. The adsorption and reactions of various atoms and molecules with $Bi_2(Se,Te)_3$ have thus been studied extensively, as they can result in changes to the TSS, doping and surface reconstruction. Here, TI surfaces are exposed to Cs, Bi, and halogens (Cl_2 and Br_2) in UHV and investigated by low energy electron diffraction (LEED), work function measurements and low energy ion scattering (LEIS). It is found that Cs lowers the work function and remains stable at small coverages but becomes mobile at larger coverages. Bi grows in a quasi bilayer-by-bilayer mode with the first Bi bilayer being strongly bonded to the TI surface. Both clean TI surfaces and Bi-covered surfaces are exposed to halogens. The clean surfaces are relatively inert to halogens, but they readily adsorb onto Bi films . The Bi is etched away when the samples are lightly annealed, restoring the clean Se- or Te-terminated surfaces.

5:40pm **SS+EM+PS+TF-ThA11 Atomically Controlled Metallation of Porphyrinoid Species with Lanthanides on Surfaces***, **Borja Cirera**,* IMDEA Nanoscience, Spain*; J. Björk,* Linköping University, Sweden*; G. Bottari, T. Torres,* Universidad Autonoma Madrid, Spain*; R. Miranda, D. Ecija,* IMDEA Nanoscience, Spain

Metallation of surface confined porphyrinoid architectures have emerged as an important research topic due to its importance for biological phenomena and potential applications including optoelectronics, nanomagnetism, sensing and catalysis.

Hereby, the in-situ design of mutant porphyrinoids, either by selection of unconventional metal centers like lanthanides or by choosing different backbones, is attracting great attention. In this talk we report our latest research regarding the metallation by dysprosium, an archetype lanthanide metal for magnetic applications, of porphyrinoid species of distinct cavity size.

On one hand, the deposition of Dy on top a submonolayer of fluorinated tetraphenyl porphyrin species on Au(111) affords the expression of three different Dy-derived compounds, which are identified as the: initial, intermediate and final metallated states. Importantly, the initial metallated complexes exhibit a narrow zero bias resonance at the Fermi level that is assigned to a molecular Kondo resonance with $T_k \approx 120$ K, which can be switched off by means of vertical manipulation.

On the other hand, the adsorption on Au(111) of an expanded hemiporphyrazine with 27 atoms in its internal cavity is investigated, showing a long-range orientational self-assembly. Furthermore, a spatially controlled “writing” protocol on such self-assembled architecture is presented, based on the STM tip-induced deprotonation with molecular precision of the inner protons. Finally, the capability of these surface-confined macrocycles to host lanthanide elements is assessed, introducing a novel off-centered coordination motif.

The presented findings represent a milestone in the fields of porphyrinoid chemistry and surface science, revealing a great potential for novel surface patterning, opening new avenues for molecular level information storage, and boosting the emerging field of surface-confined coordination chemistry involving f-block elements.

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

Thin Films Division
Room 104B - Session TF+AS+EL+EM+NS+PS+SS-ThA
IoT Session: Thin Films for Flexible Electronics and IoT

Moderators: Jesse Jur, North Carolina State University, Siamak Nejati, University of Nebraska-Lincoln

2:20pm **TF+AS+EL+EM+NS+PS+SS-ThA1 Ultraflexible Organic Electronics for Bio-medical Applications***, **Tomoyuki Yokota**, T. Someya,* The University of Tokyo, Japan **INVITED**

Recently, flexible electronics has much attracted to realize bio medical application for their flexibility and conformability [1-3]. To improve these characteristics, reducing the thickness of the device is very effective [4]. We have developed ultra-flexible and lightweight organic electronics and photonics devices with few micron substrates. We fabricated the 2-V operational organic transistor and circuits which has very thin gate dielectric layers. The gate dielectrics were composed of thin aluminium oxide layer and self-assembled monolayers (SAMs). Due to the very thin substrate and neutral position, our device shows the highly flexibility and conformability. The device doesn't be broken after crumpling.

And also we fabricated highly efficient, ultra-flexible, air-stable, three-color, polymer light-emitting diodes (PLEDs) have been manufactured on one-micrometer-thick parylene substrates. The total thickness of the devices, including the substrate and encapsulation layer, is only three micrometers, which is one order of magnitude thinner than the epidermal layer of the human skin. The PLEDs are directly laminated on the surface of skin and are used as indicators/displays owing to their amazing conformability as their superthin characteristics. Three-color PLEDs exhibit a high external quantum efficiency (EQE) (12, 14, and 6% for red, green and blue, respectively) and large luminescence (over 10,000 candelas per square meter at 10 V). The PLEDs are integrated with organic photodetectors and are used as pulse oximeter.

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3:00pm **TF+AS+EL+EM+NS+PS+SS-ThA3 Molecular Surface Chemistry for Improved Interfaces in Organic Electronics***, **Jacob W. Ciszek**,* Loyola University Chicago

Organic optoelectronic devices (OLED, OFETs, etc.) contain at least one, if not multiple instances of overlayers deposited onto organic semiconductors. The generated interface is inherently flawed with issues such as non-ohmic contact, overlayer delamination, or deposition induced damage arising. Traditionally, this is addressed by physical vapor deposition of yet another layer or by reengineering the materials in the device stack. In contrast, a reaction based approach allows for a wider range of function to be installed via molecular components in an organized and oriented manner, all while take advantage the inherent reactivity of the organic molecules which comprise the semiconducting layer. We have developed this approach via a "click-like" Diels-Alder chemistry whereby prototypical acene films (tetracene or pentacene) can be appended with a variety of small molecules to form an interfacial layer only ~5 Å thick. This chemistry is then applied towards improving the metal on semiconductor contact. As a demonstration of principle, Diels-Alder chemistry is utilized to form covalent bonds linking the organic semiconductor with a deposited metal contact thereby eliminating the poor adhesion present in this system. Application of the chemistry towards contact potential shifts is presented, while work towards sensing applications concludes the talk.

3:20pm **TF+AS+EL+EM+NS+PS+SS-ThA4 Investigation of Low Temperature ALD-deposited SnO_2 Films Stability in a Microfabrication Environment***, **Tony Maindron**, S.M. Sandrez, N.V. Vaxelaire,* CEA/LETI-University Grenoble Alpes, France

For applications such as displays (LCD, OLED) or solar cells, it is mandatory to use Transparent Conductive Oxides (TCOs) so as to allow light to extract out of the circuit or for light harvesting, respectively. In display technology, TCOs are also studied so as to replace the silicon technology developed to make the semiconducting channel in thin-film transistors. The mainstream TCO today is indium tin oxide (ITO), (90% indium oxide and 10% tin oxide). It has the advantage of having a high conductivity and a low surface resistivity, of the order of 10 ohm/square, while having a transmittance greater than 85% over the entire visible spectrum. However, it has several drawbacks, including the scarcity of indium and the high cost associated to its extraction process, which has prompted the scientific community to look for alternative TCOs. Among all TCOs, ZnO has been widely studied as a low cost single-metal oxide alternative material to ITO, as well as its multi-metal oxide derivatives using a dedicated metal dopant to control its electrical conductivity, as for instance with Al (ZnO:Al or AZO). One issue however with ZnO films lays in their relative chemical stability to water. It has been shown that films of ZnO or AZO change their physical properties when exposed to moisture: electrical conductivity decreases, roughness can increase, and optical characteristics are modified. By extension, when ZnO-based TCOs have to be finely patterned by photolithography, their high sensitivity to water-based solutions can be a severe issue. In our laboratory, we have noticed that ZnO and AZO films made by ALD at 150 °C typically are not stable in a microfabrication process: a large decrease (~ 20 %) of AZO thickness after the development step of photoresists used to pattern the TCO film has been noticed. One way to stabilize ZnO-based compounds is to anneal the films at high temperatures. However for some dedicated applications that use fragile substrates (plastic films for flexible organic electronics for instance), such post annealing processes at high temperature (typ. > 150 °C) cannot be applied. An alternative is to explore alternative materials to AZO: we found out that SnO_2 ALD (150 °C) shows very promising features regarding the stability under a microfabrication environment, while having good electrical and optical characteristics.

4:00pm **TF+AS+EL+EM+NS+PS+SS-ThA6 Dopant Distribution in Atomic Layer Deposited ZnO:Al and In_2O_3:H Films Studied by Atom Probe Tomography and Transmission Electron Microscopy***, Y. Wu, B. Macco,* Eindhoven University of Technology, The Netherlands*; A.D. Giddings, T.J. Prosa, D.J. Larson,* CAMECA Instruments Inc.*; S. Kölling, P.M. Koenraad, F. Roozeboom, **Erwin Kessels**, M.A. Verheijen,* Eindhoven University of Technology, The Netherlands

Transparent conductive oxides (TCOs) are ubiquitous in many of today's electronic devices, including solar cells. Atomic layer deposition (ALD) is a promising method to prepare high quality TCO films due to its well-known virtues – i.e., precise growth control, excellent conformality and uniformity – combined with its damage-free character. Here we report on two types of TCO films that we have studied by a combination of atom probe tomography (APT) and high-resolution transmission electron microscopy (TEM). The aim was to get more insight into how the dopants are distributed in the films.

The first study was carried out on ZnO:Al prepared by alternating cycles of $Zn(C_2H_5)_2$ and H_2O with cycles of $Al(CH_3)_3$ and H_2O in a supercycle fashion at 250 ^oC. For this material it is known that the maximum conductivity achievable is limited by the low doping efficiency of Al. To better understand the limiting factors for the doping efficiency, the 3-dimensional distribution of Al atoms in the ZnO host material matrix has been examined at the atomic scale by the aforementioned techniques [1]. Although the Al distribution in ZnO films prepared by so-called "ALD supercycles" is often presented as atomically flat δ-doped layers, in reality a broadening of the Al-dopant layers was observed with a full-width-half-maximum of ~2 nm. In addition, an enrichment of the Al at grain boundaries was seen.

The second study involved In_2O_3:H prepared by InCp and a mixture of O_2 and H_2O at 100 ^oC. This material provides a record optoelectronic quality after post-deposition crystallization of the films at 200 ^oC. Since both the H dopant incorporation and the film microstructure play a key role in determining the optoelectronic properties, both the crystal growth and the incorporation of H during this ALD process were studied [2]. TEM studies show that an amorphous-to-crystalline phase transition o ccurs in the low temperature regime (100-150 °C), which is accompanied by a strong decrease in carrier density and an increase in carrier mobility. Isotope studies using APT on films grown with D_2O show that the incorporated hydrogen mainly originates from the co-reactant and not from the InCp precursor. In addition, it was established that the incorporation of hydrogen decreased from ~4 at. % for amorphous films to ~2 at. % after the transition to crystalline films.

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4:20pm **TF+AS+EL+EM+NS+PS+SS-ThA7 Roll-to-Roll Processable OTFT Sensors and Amplifier***, **Kai Zhang**,* University of Oxford, Department of Materials, UK*; C.-M. Chen, B. Choubey, H.E. Assender,* University of Oxford, UK

The high flexibility and relatively low cost of organic electronics are gradually providing more possibility for their application. Compared with conventional silicon based electronics, organic electronics have relatively short lifecycles and processor speed, but they are more promising in the market of wearable and flexible devices, for example, wearable health care devices, simple memory devices and flexible displays. In recent years, some flexible and wearable sensors have been developed, e.g. skin-touching sensors embedded in a sports suit can detect the change of heart rate, blood pressure, ion concentration of perspiration, or infrared radiation from the human body.

In most sensors based on organic thin film transistors (OTFT) made to date, the semiconductors are employed directly to detect analytes. However, (1) the lifecycles of this design is short due to the low stability of organic semiconductors; and (2) any modification for selectivity needs to be compatible with the semiconductor.

In this paper, we present sensors based upon an extended floating gate in order to separate the sensory area from the semiconductor. Transistors are manufactured, using our roll-to-roll vacuum webcoating facility, using a high-throughput all evaporation process (Ding et al., 2016, Taylor et al., 2015). We have demonstrated the principle of operation of a floating gate sensor integrated with the vacuum-deposited OTFT, by means of a simple strain sensor, using ferroelectric PVDF on the extended floating gate to directly act as a sensory material. To amplify the sensor signal further, a series of current mirrors and differential amplifiers have been designed based on the properties of single OTFTs. The combination of organic amplifier and OTFT sensor will be helpful to transduce sensing signal to a suitable level for wireless signal reading from flexible devices.

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4:40pm **TF+AS+EL+EM+NS+PS+SS-ThA8 Functionalization of Indium Gallium Zinc Oxide Surfaces for Transparent Biosensors***, X. Du, S. John, J. Bergevin, **Gregory Herman**,* Oregon State University

Amorphous indium gallium zinc oxide (IGZO) field effect transistors (FETs) are a promising technology for a wide range of electronic applications including implantable and wearable biosensors. We have recently evaluated the functionalization of IGZO back channel surfaces with a range of self-assembled monolayers (SAM) to precisely control surface chemistry and improve stability of the IGZO-FETs. The SAMs evaluated include, n-hexylphosphonic acid (n-HPA), (3,3,4,4,5,5,6,6,6-nonafluorohexyl) phosphonic acid (FPA), and (3-aminopropyl) trimethoxysilane (APTMS). A comparison of the surface chemistry is made for bare and SAM functionalized IGZO back channel surfaces using X-ray photoelectron spectroscopy and electronic device measurements in air and phosphate buffer solution (PBS). We find significantly improved device stability with the SAMs attached to the IGZO back channel surface, both in air and PBS. We related this to the reduction of traps at the back channel surface due to SAM passivation. To further evaluate the IGZO-FETs as biosensors we have immobilized glucose oxidase (GOx) to the APTMS functionalized IGZO back channel surface using glutaraldehyde. We find that both the FPA functionalized and the GOx immobilized surfaces are effective for the detection of glucose in PBS. Furthermore, the GOx immobilized IGZO-FET based glucose sensors have excellent selectivity to glucose, and can effectively minimize interference from acetaminophen/ascorbic acid. Finally, we will discuss fully transparent IGZO-FET based glucose sensors that have been fabricated directly on transparent catheters.These results suggest that IGZO-FETs may provide a means to integrate fully transparent, highly-sensitive sensors into contact lenses.

5:00pm **TF+AS+EL+EM+NS+PS+SS-ThA9 Large Area Atmospheric Pressure Spatial ALD of IZO and IGZO Thin-film Transistors***, C. Frijters, I. Katsouras, A. Illiberi, G. Gelinck,* Holst Centre / TNO, Netherlands*; **Paul Poodt**,* Holst Centre / TNO and SALDtech B.V., Netherlands

Atmospheric pressure Spatial ALD is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. An emerging application for Spatial ALD is flat panel (OLED) display manufacturing. Examples include oxide semiconductors and dielectric layers for use in thin-film transistors (TFT's), and thin-film encapsulation for flexible OLED displays. As today's displays are fabricated on glass plate sizes in the order of several square meters, a remaining challenge is the development of large-area Spatial ALD deposition technology that is able to combine high throughput with uniform performance across very large areas.

We are developing large area Spatial ALD technology, and as a first step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm^2 sized substrates. With this tool we are able to deposit uniform films across a deposition width of 400 mm and thickness non-uniformities of ~ 1%. The whole tool is operated under an atmospheric pressure but inert N_2 environment. The tool can be used to deposit a variety of materials using both thermal and plasma-enhanced Spatial ALD.

We will present about the fabrication and performance of 30 cm x 30 cm TFT backplanes with $InZnO_x$ (IZO) and $InGaZnO_x$ (IGZO) oxide semiconductors deposited by spatial ALD. The IZO and IGZO films were deposited by plasma enhanced Spatial ALD using co-injected In-, Ga- and Zn-precursors and an atmospheric pressure N_2/O_2 plasma. The deposition process has been optimized in terms of film composition and electrical properties on a lab-scale reactor before being translated to the large area spatial ALD rector. We will report on the yield and performance of the 30 cm x 30 cm TFT backplanes, including electrical properties such as the field effect mobility, V_{on} and bias stress stability and compare it with state-of-the-art sputtered IGZO TFT's. Finally, the challenges in up-scaling Spatial ALD to plate sizes of 1.5 m and beyond will be discussed.

5:20pm **TF+AS+EL+EM+NS+PS+SS-ThA10 Thin Film Ink-Jet Printing on Textiles for Flexible Electronics***, **Jesse Jur**, I. Kim, H. Shahariar,* North Carolina State University

Inkjet printing of thin film flexible electronics on textiles is an emerging field of research with advances in wearable technology. In this study we describe for the first-time a reliable and conformal inkjet printing process of printing particle free reactive silver ink on textile surfaces. Reactive silver ink is printed on fibers with eclectic polymers ranging from polyester and polyamide, and different structures of textiles such as knitted, woven, and nonwoven fabrics. The conductivity and the resolution of the inkjet-printed tracks are directly related to the fiber structures in the fabrics. Multiple passes of printing layers are needed to confirm the percolation of the metal network on porous, uneven surfaces. The conformity and the electrical conductivity of the inkjet-printed conductive coating on PET textiles are improved by in-situ heat curing the substrate during printing and surface modification, for example, by atmospheric oxygen plasma treatments. The in-situ heat curing potentially minimizes wicking of the ink into the textile structures. We have achieved the minimum sheet resistance of 0.2 Ohm/sq on polyester knit fabric, which is comparable to the conductive thick-paste used in the screen-printed process, as well as other traditional physical and chemical deposition processes on textile fabrics/yarns. Additionally, we have constructed textile knit structures which changes electric percolation depending on structural deformations of the knit loops, providing positive and negative gauge factors upon stretching. The printed patterns are post-treated with diluted silicone/UV curable aliphatic water-soluble polyurethane coating to improve the durability during washing. These findings open up the possibility of integrating inkjet printing in the scalable and automated manufacturing process for textile electronic applications.

5:40pm **TF+AS+EL+EM+NS+PS+SS-ThA11 Flexography Oil Patterning for In-line Metallization of Aluminium Electrodes onto Polymer Webs: Commercial Roll to Roll Manufacturing of Flexible and Wearable Electronics***, **Bryan Stuart**, T. Cosnahan, A.A.R. Watt, H.E. Assender,* University of Oxford, Department of Materials, UK

Vacuum metallisation of aluminium through shadow masks has been commercially used for decades for depositing electrodes on rigid semiconductor devices, however recent developments have enabled large area, continuous deposition of patterned metallization in the aesthetic printing industry and has the potential for electrode interconnects for devices on flexible substrates such as Polyethylene Terephthalate (PET) and Polyethylene Naphthalene (PEN). Flexible polymer webs of PET were coated (*SeeSupplementary Figure*) with 50 nm thick, 165 um wide aluminium electrodes by commercially compatible manufacturing at roll-to-roll web speed of 2.4 m min^{-1} showing tremendous potential for large scale manufacturing of wearable electronic devices in transistors, low level energy generation (Thermoelectric generators), energy storage (thin film batteries) or display technologies (LED displays) [1].

The in-line patterning process relies on adaptation of flexography ink printing which typically transfers ink to a rubber patterned plate for printing images onto polymer webs. The flexibility of the printing plate accommodates for irregularities in the surface of the substrate making this process desirable for large area manufacturing. Metallization has been used to deposit aluminium onto a flexography applied pattern by replacing ink with a low vapor pressure oil (e.g. Perfluropolyether, Krytox®). The radiative heating of aluminium metallization causes simultaneous evaporation of the oil pattern, thereby rapidly forming the desired metal pattern onto the un-patterned regions. Currently we are scaling-up the oil flexography/metallization process into an industrial-scale roll-to-roll coater with potential web widths of 350 mm and roll speeds of 100 m min^{-1}, in order to increase web speeds, and to expand the range of materials deposited and the functional devices to which they are applied.

This paper reports on in-line pattern deposition of aluminium and other materials as applied to functional devices, for example organic thin film transistors and thermoelectric devices. In particular we are able to demonstrate how the process can be compatible with other functional layers. We will report our studies of electrode precision (shapes/sizes) by patterned metallization and our first studies of sputtering with flexography patterning. The long term view is integration of this technology along the R2R production path for single pass/high speed production of low cost and flexible integrated circuits.

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2D Materials Focus Topic
Room Hall B - Session 2D-ThP

2D Materials Poster Session

2D-ThP1 Activated Reduction Plasma Assisted Sulfurization in Layered WS_2 Synthesis*, **Chien-Pao Lin**, C.-N. Hsiao,* ITRC,NARL, Taiwan, Republic of China*; P.-S. Chen, C.-A. Jong,* No Matching Affiliation, Taiwan, Republic of China

CVD process is known as a promising method in large domain size and continuous 2D film synthesis. Sulfurization of Group VIB contained precursor (metal or metal oxide) for sulphide formation were widely studied. Sulfur is also reported as reduction agent of metal oxide at initial stage. In some cases, H_2 flew along with sulfur vapor during reduction time in MOCVD [1] and ALD [2] process. H_2 could be beneficial in the impurity removal and to enlarge the domain size effectively.

Plasma source in vacuum technology is useful especially in lowering the process temperature and for increasing the precursor decomposition efficiency in CVD or ALD process. R. Morrish et al., revealed that a and longer than 30 min at 500°C for sulfurization process using 10% H_2S plasma could reduce the activation energy between WO_3 and H_2S [3]. The presence of energetic radicals such as atomic S and H during sulfurization, the temperature and the exposure time are important.

In this study, we demonstrated the sulfurization process by two steps: (1) The energetic hydrogen (H*) generated by ICP plasma in WO_3 reduction at early stage, (2) Reaction between the activated hydrogen (H*) and sublimated sulfur vapor for WS_2 formation. The hydrogen concentration, plasma exposure time, the reaction temperature and duration time are evaluated for the sulfurization of WO_3.

WO_3 film was deposited on Si substrate covered by 90 nm thermal dry oxide. Samples were sulfurized in a 4 inch inductively coupled plasma (ICP) reactor with copper coil connected to a 13.56 MHz RF power supply. The reaction temperature varied from 700 to 900°C. Raman and PL spectrum were adopted for the film quality inspection. The surface roughness of formed WS_2 layers were examined by AFM. The best condition performed when the reaction temperature was 850°C with 5% H_2 plasma pre-treatment for 20min. Higher H% is harmful for film formation, which was similar to the report by K. N. Kang et al. that sulfurization can etch the damage of the film [4]. Raman and photoluminescence (PL) spectroscopy were taken with 532 nm excitation. The uniform Raman signals and PL spectrum within 4 cm^2 are shown and the center of the PL peak was at 629 nm (1.97 eV).

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2D-ThP2 Quantized States, Berry Phases, and Quantum-Hall Wedding-Cake structures in Graphene Quantum Dots*, **Fereshte Ghahari Kermani**, D. Walkup, C. Gutiérrez,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; C. Lewandowski,* Department of Physics, Massachusetts Institute of Technology*; J. Rodriguez-Nieva,* Massachusetts Institute of Technology*; K. Watanabe, T. Taniguchi,* National Institute for Materials Science, Japan*; L. Levitov,* Massachusetts Institute of Technology*; N.B. Zhitenev, J.A. Stroscio,* National Institute of Standards and Technology (NIST)

Recent progress in creating and probing graphene quantum dots (QDs) with fixed build-in potentials has offered a new platform to investigate Klein tunneling related phenomena . In this talk, I describe scanning tunneling spectroscopy measurements of the energy spectrum of graphene QDs as a function of energy, spatial position, and magnetic field. In the absence of a magnetic field, confinement of graphene carriers in a *p-n* junction resonator gives rise to a series of quasi-bound single particle states which result from oblique Klein scattering at the *p-n* interface. Applying a weak magnetic field, we observe a giant and discontinuous change in the energy of time-reversed angular-momentum states, which manifests itself as the appearance of “new” resonances in the tunneling density of states. This behavior corresponds to the on/off switching of a π- Berry phase when a weak critical magnetic field is reached. With increased applied magnetic field, the QD states can be confined even further as they condense into highly degenerate Landau levels providing the first spatial visualization of the interplay between spatial and magnetic confinement. This is observed as formation of the seminal wedding-cake structures of concentric compressible and incompressible density rings in strong magnetic fields.

2D-ThP3 Growth Phenomena and Mechanism of MoS2 Formed by Conventional Chemical Vapor Deposition*, **Cheol-Min Hyun**, J.H. Choi, S.W. Lee, J.-H. Ahn,* Korea Maritime and Ocean University, Republic of Korea

In recent years, transition metal dichalcogenide (TMDC) compound, have heen studied as a platform for next generation semiconductor devices. One of the most representative two-dimensional TMDC materials, MoS2 is applied as a device as well as various synthesis methods are known, including chemical vapor deposition. However, in-depth research on the synthesis process and the mechanism of the variable has not been done yet. Therefore, in this study synthesis of single layer MoS2 by using conventional chemical vapor deposition, as MoO3 and sulfur powder, we observe and discuss the synthesized crystal shape on the substrate, according to the distance of sulfur and MoO3. The synthesized nano-crystals were characterized by optical microscopy (OM), x-ray diffraction (XRD), raman spectroscopy. Fig. 1. shows the OM-image and raman spectra of synthesized MoS2, MoO2 crystals on S1 and S2 substrate, respectively. MoS2 crystals are synthesized on the S1 substrate close to the sulfur source, MoO2 crystals are synthesized on the S2 substrate. From these results, we were able to studies the mechanism of MoS2 synthesis. In the synthesis of MoS2, using a MoO3 and sulfur powder, the synthesis mechanism was shown as a schematic of the various experiments and in-depth understanding.

Therefore, we have demonstrated that the importance of MoO2 formation as the intermediate phase in MoS2 synthesis using MoO3 and sulfur powder. And then, the MoS2 synthesis mechanism was easier to understand through the schematic illustration.

2D-ThP4 Graphene Micro Wires Defined by Photolithography and Plasma Etching for Field Effect Transistors*, F.C. Rufino, A.M. Pascon,* University of Campinas, Brazil*; D.G. Larrude,* Mackenzie Presbyterian University, Brazil*; W.C. Mariano, **José Alexandre Diniz**,* University of Campinas, Brazil

With the need of the development of smaller devices, the search for materials with physical and chemical properties favorable to these advances has become a priority. However, Moore's Law is no longer verified [1], reinforcing research into new technologies, with a strong focus on 2D materials. The graphene, a 2D material, composed of sp2 hybrid carbon atoms, emerges as a strong candidate in nanotechnology applications due to its outstanding electronic properties, high electrical conductivity, mobility, flexibility, mechanical strength and transparency [2], making it the ideal material to replace the silicon in the traditional FETs.

We report the fabrication of transistors based on graphene channel (GraFETs), applying the photolithography and oxygen plasma etching processes to define the graphene channel region, creating ten micro wires, which are parallel connected, at the same device, as FinFET transistors based on silicon nanowires. Usually, the graphene channel region is not formed by the wires in parallel, but by square or rectangular shapes. Devices, with wires in parallel, can get an increase in drain-source current and the transconductance response, which can improve the sensitivity of sensors based on GraFETs. Thus, in this work is presented the fabrication of GraFETs with: i) High quality CVD (Chemical vapour deposition) monolayer graphene, which was transferred on the GraFETs; ii) The channel, with total width of 3.6 µm, was formed by ten micro wires in parallel, with each width of about 0.36 µm, (obtained by lithography and O_2 plasma etching).

The Raman spectroscopy was used to investigate the integrity of graphene structure on GraFETs during the fabrication. The Scanning Electron Microscopy (SEM) was used to show the channel formation with ten graphene wires and to measure the dimensions of these wires. The drain-source current versus drain-source voltage, the drain-source current versus gate voltage, and the transconductance versus gate voltage, were extracted to evaluate the electrical characterization of our GraFETs. The graphene used in the manufacture of the transistor was obtained through CVD, where the graphene is grown on a copper substrate by surface catalysis of the CH_4 and H_2 gases [3]. The growth process is done in a CVD chamber with a vacuum of 10^{-3} torr and a temperature of 1000 ºC, the transference of CVD monolayer graphene on the device region using wet transfer method and PMMA as a supporting layer [4].

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2D-ThP6 In-Operando AFM/STM and Transport Measurements of a Graphene Hall Bar Device*, **Johannes Schwenk,*** National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; S. Kim,* National Institute of Standards and Technology (NIST) / Department of Physics and Astronomy, Seoul National University, Seoul, Korea*; F. Ghahari,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; J. Berwanger,* Institut für Experimentelle und Angewandte Physik, Universität Regensburg, Germany*; W.G. Cullen, S.R. Blankenship,* National Institute of Standards and Technology (NIST)*; Y. Kuk,* Department of Physics and Astronomy, Seoul National University, Seoul, Korea*; F.J. Giessibl,* Institut für Experimentelle und Angewandte Physik, Universität Regensburg, Germany*; N.B. Zhitenev, J.A. Stroscio,* National Institute of Standards and Technology (NIST)

We present initial studies of a backgated graphene Hall bar device using simultaneous measurements of atomic force microscopy (AFM), scanning tunneling microscopy (STM) and electronic transport. Laterally resolved spectroscopy with high energy resolution is used for the investigation of exotic ground states and edge channels within the two-dimensional graphene electron system, which enables us to explore links between the local microscopic behavior of the device and its mesoscopic transport properties.

A recently constructed microscope uses a self-sensing quartz sensor (qPlus) and operates in an ultra-high vacuum (UHV) environment inside a dilution refrigerator (DR) with a base temperature of 10 mK and magnetic fields up to 15 T [1]. Radio frequency (RF) filtering of all signal lines entering the UHV chamber and improved home built RF powder filters at the 10 mK stage were implemented to produce an improved energy resolution in tunneling spectroscopy. Low noise preamplifiers for the sensor deflection [2] and the STM current signal [3] were implemented at the 4 K stage within the DR. This allows for reduced Johnson noise of the amplifier feedback resistors and a relatively short distance (1.2 m) between amplifier and the STM/AFM module where the sensor is operating. In this poster we describe aspects of the instrumentation and initial measurements of the graphene Hall bar device.

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Actinides and Rare Earths Focus Topic
Room Hall B - Session AC-ThP

Actinides and Rare Earths Poster Session

Moderators: David Shuh, Lawrence Berkeley National Laboratory, James Tobin, UW Oshkosh

AC-ThP1 Upconversion Photoluminescence Efficiency Dependence of Yb ions in Gd0.91-xNbO4: Ybx3+, Er0.09*, S.S. Yi,* ***Seung Gon Lee,*** Silla University, Republic of Korea

$Gd_{(0.91\text{-}x)}NbO_4$: $Er^{3+}_{0.09}$, Yb^{3+}_x (x= 0.03, 0.06, 0.09, 0.12 and 0.15) phosphors were synthesized by the facile solid state reaction method. Yb^{3+} concentrations were changed from 0.03 to 0.15 mol for the fixed Er^{3+}concentration at 0.09 mol. The particle size of phosphors was around 180 ~ 350 nm and shape were angular oval observed by scanning electron microscopy. The crystalline structures of the phosphors were investigated by X-ray diffraction. The photoluminescence emission based on the green emissions near 528 and 551 nm and red emissions near 657 and 675 nm were observed and the highest emission intensity occurred for the sample $Yb_{0.15}$ $Er_{0.09}$. Also, under the 980 nm excitation, Er^{3+}, Yb^{3+} co-doped $GdNbO_4$ phosphors appeared the up-conversion emission based on the green emission near 535 nm and 556 nm radiated by $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions and red emission about 657 nm and 675 nm radiated by $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition, which assigned to the intra 4f transitions of Er^{3+} ions.

AC-ThP2 Luminescence Characteristics of $(Gd_{0.85\text{-}x}Yb_{0.15})NbO_4$:$Er_x^{3+}$ Phosphors*, S.S. Yi,* ***DongGyu Lee,*** Silla University, Republic of Korea

$Gd_{(0.85\text{-}x)}NbO_4$: $Yb^{3+}_{0.15}$, Er^{3+}_x (x= 0.03, 0.06, 0.09, 0.12 and 0.15) phosphors were synthesized by the solid state reaction method. Er^{3+} concentrations were changed from 0.03 to 0.15 mol for the fixed Yb^{3+}concentration at 0.15 mol. The crystalline structures of the phosphors were investigated by X-ray diffraction. The particle size of phosphors was around 140 ~ 320 nm and shape were angular oval observed by scanning electron microscopy. The photoluminescence emission based on the blue emission near 471 nm, green emission near 596 nm and red emission near 621 nm were observed and the highest emission intensity occurred for the sample $Yb_{0.15}$ $Er_{0.09}$. Also, under the 980 nm excitation, Er^{3+}, Yb^{3+} co-doped $GdNbO_4$ phosphors appeared the up-conversion emission based on the green emission near 535 nm and 556 nm radiated by $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions and red emission about 657 nm and 675 nm radiated by $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition, which assigned to the intra 4f transitions of Er^{3+} ions.

AC-ThP3 Exploring the Electronic Structure of Molecular Lanthanide Complexes in the +2 Oxidation State Using Photoelectron Spectroscopy*, **Daniel Huh**, J.P. Bruce, J.C. Hemminger, W. Evans,* University of California, Irvine

Recent advances in rare-earth metal reduction chemistry have led to the isolation of a new series of Ln(II) complexes. For Ln = Y, La, Ce, Nd, Gd, Tb, Dy, Ho, Er, and Lu, reduction of $4f^n$ $(C_5H_4SiMe_3)_3Ln^{III}$ complexes generates $[(C_5H_4SiMe_3)_3Ln^{II}]^{1-}$ products that exhibit unusual $4f^n5d^1$ mixed-principal quantum number electron configurations. X-ray photoelectron spectroscopy (XPS) has been employed to examine and compare these mixed-principal quantum number electronic structures with those of traditional Ln(II) complexes that have $4f^{n+1}$ configurations. In this work, X-ray and ultraviolet photoelectron spectroscopy have been used to examine the electronic structure of $[K(2.2.2\text{-cryptand})][(C_5H_4SiMe_3)_3Ln^{II}]$ (Ln = Eu, Gd, Tb) where Gd(II) and Tb(II) have previously been shown to have non-traditional $4f^75d^1$ and $4f^85d^1$ electronic configurations, respectively, and where Eu(II) has been shown to have a traditional $4f^7$ electronic configuration.

AC-ThP5 Magnetism of the $(Nd,R)_2Fe_{14}B$ - H system with R = Er and Tm*, I. Tereshina,* ***Lev Ivanov,*** M.V. Lomonosov Moscow State University, Russian Federation*; D. Gorbunov,* Helmholtz-Zentrum Dresden-Rossendorf, Germany*; M. Paukov,* Charles University, Prague, Czech Republic*; E.A. Tereshina-Chitrova,* Institute of Physics, Academy of Sciences of the Czech Republic*; M. Doerr,* Technische Universität Dresden, Germany*; L. Havela,* Charles University, Prague, Czech Republic*; A.V. Andreev,* Institute of Physics ASCR, Czech Republic

Since the discovery in 1984, the $R_2Fe_{14}B$ (R is a rare earth) compounds received a considerable scientific attention due to their hard magnetic properties [1,2]. Fundamental characteristics of the best permanent magnet $Nd_2Fe_{14}B$ are known to be highly sensitive to the atomic substitutions and absorbed light atoms such as hydrogen. In the present work, we studied a combined influence of substitutions of Er and Tm for Nd and hydrogen absorption on the behavior of magnetization in magnetic fields up to 60 T. All studies were conducted on free powder samples at 2 K.

It is found that the substitution in the rare earth sublattice decreases the saturation magnetization as a result of ferrimagnetic ordering of magnetic moments of heavy rare earths with respect to the moments of Nd and Fe. However, under sufficiently strong magnetic fields the magnetic moments rotate and in the ideal case, the field-induced ferromagnetic state is observed. This phenomenon is directly connected to the strength of the inter-sublattice exchange interactions (Fe and Nd, Er, Tm sublattices).

In the parent materials $(Nd_{0.5}Er_{0.5})_2Fe_{14}B$ and $(Nd_{0.5}Tm_{0.5})_2Fe_{14}B$ in fields up to 60 T no increase of the magnetization was observed. Hydriding of the compounds up to the maximum possible hydrogen content 5.5 at.H/f.u. allows us to observe a forced-ferromagentic state in the $(Nd_{0.5}Tm_{0.5})_2Fe_{14}BH_{5.5}$ compound. The transition from ferri- to the ferromagnetic state occurs gradually: it begins at the 35 T field and finishes at 55 T. For the compound $(Nd_{0.5}Er_{0.5})_2Fe_{14}BH_{5.5}$ we also observe a magnetization increase. So that, hydrogenation is found to weaken the intersublattice exchange interaction in these three-sublattice materials.

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[1] J. F. Herbst, Rev. Mod. Phys . 63, 819 (1991).

[2] O . Gutfleisch et . al . Advanced Mater . 23 (7), 821 (2011).

Applied Surface Science Division
Room Hall B - Session AS-ThP
Applied Surface Science Division Poster Session

AS-ThP1 Toward an Improved Understanding of the role of soil organic matter in NOy cycling through Investigation of Heterogeneous Reactions with NO2+*, R. Hansen,* Indiana University*; **Mark Engelhard,*** Pacific Northwest National Laboratory*; J. Raff,* Indiana University

Molecular level investigation of compositional changes due to heterogeneous reactions of nitrogen oxides (NO_x, NO_y) with soil organic matter (SOM) is important to develop a fundamental scientific understanding of the soil/atmosphere interface. In addition, interactions between NO_x reservoir species and SOM play a more important role in NO_x and NO_y recycling than previously realized. Despite the importance of soil to the global terrestrial-atmospheric cycling of nitrogen, interactions of N_2O_5 with SOM are not well understood. Uncertainty in these processes is problematic because it means that NO_y is not properly represented in the Earth-systems models used for prediction and regulation. The ultimate objective of this study is to investigate the production of NO_y from the reaction of N_2O_5 with SOM and elucidate the mechanisms that return NO_y back to the atmosphere, where NO_y can contribute to aerosol and O_3 formation. In the initial phase of this study, we reacted SOM standards with NO_2^+ (produced from concentrated HNO_3), which is an intermediate in the heterogeneous reaction of N_2O_5 with SOM. We then characterized these reaction products using X-ray photoelectron spectroscopy (XPS). XPS was used to measure the nitrogen chemistry before and after reaction of SOM with NO_2^+. These results will be discussed along with the pros and cons using XPS to characterize SOM chemistry.

AS-ThP2 Measuring the Damage Depth and Recovery of PEMA Thin Films using Multiple Technique Analysis*, **William Sgammato**, R.E. Simpson,* Thermo Fisher Scientific, UK

Sputtering polymer surfaces with monatomic Ar ions is known to induce changes in the polymer chemistry. PEMA in particular, is a "self-sealing" polymer type which means during Ar^+ sputtering cross-linking occurs. The advantage of using Ar cluster ions is that such chemical changes are not induced. It has also been demonstrated that Ar^+_n ions can be used to remove the damage layer produced by Ar^+ ions, thus recovering the surface chemistry. In this investigation this ability to recover the polymer surface is used to measure the relative thickness of the damage layer produced by Ar^+ ions. To facilitate this other techniques were used for film thickness measurement and calibration. AFM was used to accurately measure the thickness of the PEMA film, this data was then used to calibrate a separate scale that was used to estimate the thickness based on the colour of the surface. As the colour of the surface is dependent only on the refractive index of the material, the angle of incidence of the incoming light and the thickness of the film, the measurements can produce a high accuracy thickness estimate to within ± 10 nm. The estimate of the original film thickness, made using the film colour, ~ 400 nm was in good agreement with the average thickness measured using AFM 398 nm.

The results of this investigation showed that the relative depth of damage induced by a 3 keV Ar^+ ion beam in a PEMA thin film was 245 ± 10 nm. Film thickness measurements were also used to calibrate Ar^+ and Ar^+_n etch rates which were calculated as 0.94 and 2.60 nm/s respectively. The low Ar^+ etch rate was an indication of sample cross-linking during etching.

AS-ThP3 Determination of Band Offsets in Semiconductor Heterostructures (2D/3D) by using XPS*, **Mohamed Hedhili**,* King Abdullah University of Science and Technology (KAUST), Core Labs, Saudi Arabia*; M. Tangi, P. Mishra, T.K. Ng, B. Janjua, C.C. Tseng,* Photonics Laboratory, King Abdullah University of Science and Technology (KAUST), Saudi Arabia*; D.H. Anjum,* King Abdullah University of Science and Technology (KAUST), Core Labs, Saudi Arabia*; M.S. Alias,* Photonics Laboratory, King Abdullah University of Science and Technology (KAUST), Saudi Arabia*; N. Wei,* King Abdullah University of Science and Technology (KAUST), Core Labs, Saudi Arabia*; L.J. Li,* Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Saudi Arabia*; B.S. Ooi,* Photonics Laboratory, King Abdullah University of Science and Technology (KAUST), Saudi Arabia

Heterojunctions are generally formed at the interface of different energy-gap semiconductor materials due to their mismatching electron energies in the valence bands. The values of valence-band mismatches or offsets hold a great significance for the optoelectronics applications and hence their accurate determination is of paramount importance. High-resolution X-ray photoemission spectroscopy (HR-XPS) is proven to be a powerful way of measuring the valence band offsets in such semiconductor heterojunctions. In this report, we extend HR-XPS studies for such measurements to 2D/3D types of heterojunctions. These 2D/3D junctions are synthesized by combining 3D semiconductors (e.g. GaN or InAlN) with 2D semiconductors (e.g. WSe_2 or MoS_2). By performing an elaborate XPS analysis, we are able to show the type of heterojunctions formed by these semiconductor materials. For instance, we observed that the heterojunction of GaN with either MoS_2 or WSe_2 is of “Type-II”. Whereas, the junction of InAlN with MoS_2 is “type-I”. The presented HR-XPS results are both supported and corroborated by performing the analaysis of these samples with other techniques including atomic force microscopy, scanning transmission electron microscopy, micro-Raman, absorbance, and microphotoluminescence . The band alignment parameters determined here provide a route toward the integration of group III nitride semiconducting materials with transition metal dichalcogenides (TMDs) for designing and modeling of their heterojunction-based electronic and optoelectronic devices.

AS-ThP4 Multi-technique Characterization of Nanowire-based Catalysts and Electrodes*, **Sarah Zaccarine**, C. Ngo,* Colorado School of Mines*; S. Shulda, S. Mauger, S.M. Alia, K.C. Neyerlin, B.S. Pivovar,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines

In response to the increasing anthropogenic impact on the environment, it is vital to implement sustainable solutions to meet global energy demands. Polymer electrolyte membrane fuel cells (PEMFCs) are a promising option but the sluggish oxygen reduction reaction at the cathode leads to issues with cost and efficiency. Pt nanoparticles supported on high surface area carbon (Pt/HSC) are commonly used but suffer performance losses and do not meet Department of Energy targets for durability or cost. Extended surface nanostructures are a promising alternative as they show improved specific activity and durability. We have developed extended surface nanowire-based platinum nickel catalysts with durability, mass activity, and specific activity superior to Pt/HSC. Since the catalyst functions differently under altered conditions, it is crucial to study the catalyst at all stages as it transitions from a powder to a membrane electrode assembly (MEA), which requires a multi-technique approach.

The catalyst was studied as a powder, ink, fresh MEA, and tested MEA to determine the changes that occur as the catalyst is integrated into a full MEA. Several spectroscopy and microscopy techniques were utilized to address all relevant length scales (from atomic to micrometers). First, the catalyst was investigated using a combination of extended x-ray absorption fine structure (EXAFS) spectroscopy, x-ray photoelectron spectroscopy (XPS), scanning transmission electron microscopy (STEM) with energy dispersive x-ray spectroscopy (EDS) hypermapping, and atom probe tomography (APT) to obtain detailed information about distribution of platinum and nickel, discerning differences between surface and bulk speciation at nanometer and sub-nanometer scale. This detailed information about surface speciation was then used to better understand oxygen adsorption behavior of these catalysts, investigated using near-ambient pressure XPS (nAP-XPS). Second, evolution of the catalyst and catalyst-ionomer interface when incorporated in an electrode were examined with STEM/EDS and x-ray tomography. These studies offer invaluable insight into structure-performance relationships of the nanowire-based catalysts and development of efficient electrodes.

AS-ThP6 Characterization of Laser-Treated Ti-6Al-4V-Surfaces*, **Harry Meyer**, D. Leonard, A. Sabau,* Oak Ridge National Laboratory

Lightweight Al, Mg, and Ti alloys are ubiquitous in aerospace and automotive applications. When these alloy materials are joined, either to similar or dissimilar materials, the chemical and physical state of the surface determines the quality of the bond. Methods for cleaning (chemical) and texturing (physical) metal alloy surfaces prior to joining or paining have traditionally relied on aggressive chemicals that are now considered environmentally unfriendly. Costs for adequately protecting of worker and protecting the environment are high enough that alternate surface processing methods are needed. During the last two years ORNL, began a systematic study of a unique laser processing method for both cleaning and texturing metal surface simultaneously. This novel surface treatment method uses laser interferometry produced by two beams of a pulsed Nd:YAG laser. Operating at 10Hz of frequency, this technique has been used to clean aluminum surfaces, and at the same time creating periodic and rough surface structures. Preliminary results for the Al-alloy laser-based surface treatment process were reported last year at this conference. One of the primary findings for Al-alloy surfaces was the development of an enhanced oxide surface region. Influence of the enhanced oxide on both adhesive joining and corrosion protection are now underway. Recently, we have extended these laser-processing studies to Ti-6Al-V4 (Ti64) alloys, which are widely used in the aerospace industry. Ti64 alloy surfaces can be cleaned using high-energy laser pulses (nanoseconds to milliseconds range) and, as with the Al-alloys, is accomplished mainly by surface melting and ablation. Our method is non-contact, does not rely on surface abrasion and significantly reduces the chemical impact of commonly used solvents and detergents. The process being optimized at ORNL uses a 2-beam method that not only cleans the surface for joining but textures the surface in a periodic manner. This poster present preliminary surface characterization results for the cleaning of Ti64-alloy surfaces. Results from scanning transmission electron microscopies, x-ray photoelectron spectroscopy, and contact angle measurements on as received and laser–treated commercial Ti64-alloy surfaces will be presented. This abstract has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

AS-ThP7 Cross-Sectional Mapping vs. Depth Profiling Analysis: Is the Choice Always Clear?, ***Kathryn Lloyd***, *J.R. Marsh,* DuPont Corporate Center for Analytical Sciences

Differences in chemistry across monolithic or multi-layered films are often critical to product performance. Each component in a formulation serves a purpose. It is important to be able to monitor the integrity of multi-layered structures, the striation or migration of components, the enrichment of components at interfaces, and the formation of buried defects.

Approaches used to obtain this information can be broadly separated into cross-sectioning (combined with chemical mapping) and depth profiling (with or without chemical mapping). Cross-sectioning calls for more labor up front to prepare the samples – potting in epoxy; microtoming -- but the resulting cross-sectional surfaces are amenable to multiple chemical mapping techniques, such as Raman microprobe, secondary ion mapping, and Energy Dispersive Spectroscopy (SEM/EDS), all of which exhibit comparable lateral resolution (around 1 micron). Depth profiling requires little to no sample preparation and offers higher depth resolution (10s of nanometers).

To a large degree, film and/or layer thickness determine the approach pursued. Practical depth profiling historically has not extended much more than 10 microns into a surface. Thus, for multilayer films with thicknesses on the order of 25 microns or more, cross-sectioning has been preferred. This can present problems for surface chemical mapping techniques such as ToF-SIMS, when even cryo-microtoming can result in a thin overlayer of smeared epoxy components covering the surface.

The advent of new gas cluster ion beam (GCIB) sputter sources has not only enabled cross-sectional ToF-SIMS mapping analysis for layered and heterogeneous organic systems, but has also made the choice between cross-sectioning and depth profiling not as clear. GCIB depth profiling through organic or polymeric material can be very efficient, making the idea of profiling through 25 microns or more not as impractical as it once was.

This presentation will show examples of cross-sectional mapping analysis and sputter depth profiling, exploring which factors can influence the choice of approach and illustrating some of the trade-offs involved.

AS-ThP8 Investigation on Human Evidences using ToF-SIMS Combined with Advanced Matching Recognition, *T. Terlier,* Korea Institute of Science and Technology*; J. Lee, M. Kang,* ***Yeonhee Lee***, Korea Institute of Science and Technology, Republic of Korea

The expansion of the use of forensic sciences requires to develop new techniques providing prompt and reliable information. In terms of chemical analysis, the useful information ranges from trace elements, e.g. the elemental detection of residues in a specimen, to molecular information, e.g. the identification of high mass molecules. Time-of-Flight Secondary Ion Mass Spectrometry is able to provide a detailed 3D view of the elemental and molecular composition of solid samples and has already been used previously to analyze inorganic, organic and biological specimens, showing its strong potential to retrieve more information from trace evidence than the traditional methods.

Several challenges still prevent a widespread application of ToF-SIMS to forensic analysis. Samples from the human body are the most commonly collected specimens and these samples are particularly challenging for analysis due to the variety of specimens, including hair, fingerprints, fingernails and lipstick, and the complexity of the samples that can contain blood, saliva and/or sweat. A common material to almost all of the human specimens is cosmetics, which can provide crucial information about an individual. Through analysis of five different types of cosmetics - hair styling products, lipstick, lotion, nail polish, and foundations, we have collected a large range of ToF-SIMS spectra and build a cosmetic database from these reference samples.

The characterization of different types of human evidences has been performed to illustrate the large range of the possibilities given by the ToF-SIMS. However, to identify the chemical composition of the cosmetic residues and to determine their origins, advanced methods of classification and discrimination need to be applied. For example using Principal Component Analysis, it was possible to identify the cosmetic residues present on hair cuticles and to discriminate the hair product applied from a list of 16 references. Nevertheless, quantitative analysis can be required for identifying the exact nature of the residues. Thus, a new method combining Matching Factor and decision tree has been developed. Fingerprint analysis has been performed to identify the traces of residues contained in the fingerprint, which have also highlighted the fingerprint's ridges. After PCA segmentation, the extracted mass spectrum from the residue's region has been evaluated using a new matching recognition method, which has clearly indicated the origin of the cosmetic product.

The development of matching recognition method and the analysis performed on the human evidences has demonstrated that the ToF-SIMS is a promising way to help the forensic investigations.

AS-ThP10 Wafer Bonding Between LiTaO3(100) and Alpha-quartz SiO2(100) via Low Temperature (<220°C) NanoBonding™ Using Surface Energy Modification, ***Brian Baker***, *J. Kintz, A. Yano, N. Herbots,* Arizona State University*; W.-L. Lee,* Cactus Materials, Inc.*; S.R. Narayan, J.M. Day,* Arizona State University*; R. Islam,* Cactus Materials, Inc.*; Y. Watznabe,* TDC Coporation*; M. Koury, M. Johnson, R.J. Culbertson, M. Magnus,* Arizona State University

Wafer bonding is displacing heteroepitaxy in the manufacture of heterostructures, such as tandem solar cells and sensors. High costs and poor yields limit effective production of opto-electronic devices and sensors.

In this work, piezoelectric LiTaO3(100) and alpha-quartz SiO2(100) wafer bonding is investigated via NanoBonding™ near 300K [1,2]. NanoBonding™ generates molecular bonds between surfaces at the nanoscale over large interfacial domains, creating a 2D bonding interphase between the two materials. First, electron exchange is created between surfaces by engineering a key hydrophilic-hydrophobic surface pairs (via wet chemical processes, spin, vapor, or plasma etching). This method catalyzes electronic exchange and bonding by modifying native surfaces to a less stable state where electronic displacement is enhanced. Surface Energy Modification is measured via the surface total energy γT, and its three components γLW, γ+, γ-. These values are based on the Van Oss-Chaudury-Good (vOCG) theory, and using high resolution Three Liquid Contact Angle analysis. A key feature of Surface Energy Modification for NanoBonding™ is the creation of 2D precursor phases on surfaces. Next, for nanocontacting, the surface has to be planarized at the macro, micro, and nano scales. Last, NanoBonding™ activation can occur on contact and/or after thermal activation.

NanoBonding™ depends thus on the control of surface energy, planarity at three scales, and composition. γT can be computed from 3LCAA. The liquids used are 18 MO water, glycerin, and α-bromo-naphthalene (10 10 µL droplets). The average γT, across as received 4" LiTaO3 wafer is 43.3 ± 2 mJ/m2 (hydrophobic). However, the electron acceptor energy Y(-) can vary from 43 mJ/m2 to 23 mJ/m2 (~50% difference). Regions with low Y(-) (low electron transfer) do not bond while those high Y(-) do. This correlates directly with bonded interfacial regions visualized when LiTaO3 wafer is nano-contacted with 4" quartz wafers. In this way, 3LCAA can determine one cause of bonding failures.

Thermal activation (100 and 200°C) does not enhance bonding as significant thermal expansion causes mismatch fractures, interface delamination, or thermal decomposition due to the high mobility of Li ions.

In conclusion, thermally or plasma activated wafer bonding is clearly not optimal for wafer bonding LiTaO3. To Si-based materials, causing high fracture rates for LiTaO3 as well Li out diffusion. Instead, Nanobonding(TM) is more appropriate due to a reduced fracture or thermal decomposition chance.

Herbots N. et al. US Pat. No 9,018,077 (2015), US Pat. No 9,018,077 (2017)

Herbots N., Islam R., US Pat. Pending (2018), filed March 18, 2018

AS-ThP11 Structural, Morphological and Electrical Properties of Multilayer Sequentially Sputtered Nb_3Sn Films for Different Layer Thicknesses*, Md. Nizam Sayeed,* Old Dominion University*; U. Pudasaini,* College of William and Mary*; H. E. Elsayed-Ali,* Old Dominion University*; G. Eremeev,* Thomas Jefferson National Accelerator Facility

Nb_3Sn is an intermetallic compound of A15 crystal structure that has type II superconductivity. Due to higher critical temperature T_c = 18.1 K and upper critical magnetic field of up to 30 T, Nb_3Sn is considered as an alternative of niobium for Superconducting Radio Frequency (SRF) applications in particle accelerators. Nb_3Sn coating on the inner surface of niobium SRF cavities can be operated at 4.2 K, whereas standard niobium cavities are currently operated at 2 K and consequently reduce the operation cost. However, synthesis of Nb_3Sn is challenging due to the availability of other phases of niobium and tin (Nb_6Sn_5 and $NbSn_2$), which have poor superconducting properties. We have fabricated Nb_3Sn films on sapphire using multilayer sequential sputtering. Several thin layers of Nb and Sn were deposited repeatedly by magnetron sputtering and annealed afterward at 950 °C for 3 hours to form Nb_3Sn. We have varied the Nb and Sn layer thicknesses of the films and characterized their crystal structure by X-ray diffraction (XRD), surface morphology by scanning electron microscopy (SEM), surface topography by atomic force microscopy (AFM), film stoichiometry by energy dispersive X-ray spectroscopy (EDS). The films showed crystalline structures of Nb_3Sn only. T_c up to 17.63 K with sharp superconducting transition has been achieved.

Electronic Materials and Photonics Division
Room Hall B - Session EM-ThP

Electronic Materials and Photonics Division Poster Session

EM-ThP3 Thermal Engineering for High-Power, Flexible Electronics*, Katherine Burzynski,* University of Dayton and Air Force Research Laboratory, Materials and Manufacturing Directorate*; E.W. Blanton, N.R. Glavin, E.R. Heller, M. Snure, E.M. Heckman,* Air Force Research Laboratory*; C. Muratore,* University of Dayton

Consumers and military personnel are demanding faster data speeds only available through fifth generation (5G) wireless communication technology. Furthermore, as wearable sensors and other devices become more ubiquitous, devices demonstrating enhanced flexibility and conformality are necessary. A fundamental challenge for flexible electronics is thermal management. Even on rigid substrates with significantly higher thermal conductivity than polymeric and other flexible substrates, the full potential of semiconducting materials is often thermally limited. The flexible gallium nitride (GaN) high electron mobility transistors (HEMTs) employed in this work are grown on a two-dimensional boron nitride (BN) release layer that allows the conventionally processed devices on sapphire wafers to be transferred using a polymeric stamp and placed onto a variety of rigid and flexible substrates. Characterization of the GaN device behavior on the as-grown sapphire wafers (prior to transfer) provide a baseline for evaluation of the thermal performance of engineered interfaces and substrates. With conventional substrates, device performance (specifically, the saturation current) is reduced when the device is transferred to polymeric substrates. The thermal dissipation is further restricted due to the addition of an adhesive layer to the substrate. Thermal imaging of devices in operation reveals that the current passing through an as-grown GaN transistor on a sapphire wafer reaches the target operating temperature at approximately five times the power of the same device transferred to a flexible substrate. Printable, thermally conductive nanocomposites integrating 1D, 2D, and 3D forms of carbon in a flexible, photocurable polymer matrix, as well as metal nanoparticles, were developed to maximize heat transfer from GaN devices. The thermal conductivity of the candidate substrate materials was measured experimentally, and the performance of devices transferred to these novel flexible composite substrates was characterized. The measured thermal data was used in computational simulations to predict flexible substrate architectures effectively promoting point-to-volume heat transfer to improve device performance. Additive manufacturing for engineered architectures of the flexible, thermally conductive substrate materials was demonstrated to substantially reduce the thermal limitation of high-power flexible electronics.

EM-ThP4 Growth and Magneto-optical Properties of $ZnO/Zn_{1-x}Mn_xO$ Thin Films on Si Substrates*, Da-Ren Liu,* ITRC,NARL,Taiwan, Republic of Korea*; C.-J. Weng,* ITRC,NARL, Taiwan, Republic of Korea

ZnMnO is one of the most promising diluted magnetic semiconductors (DMS) materials due to its predicted above room temperature ferromagnetism. In this study, ZnO layer was conformally deposited on the Si substrates by atomic layer deposition (ALD). Then the $Zn_{1-x}Mn_xO$ ($0.01 < x < 0.10$) coatings were grown on ZnO layer by Nd:YAG pulsed laser deposition (PLD). The thickness and roughness of the films were characterized by grazing-incidence x-ray reflectivity (GIXR). According to the results of high-resolution x-ray diffraction, the ZnO/ $Zn_{1-x}Mn_xO$ thin films are polycrystalline with a preferential growth direction of (002). The surface and cross-section morphologies of films were analyzed by the field-emission scanning electron microscope (FE-SEM). Photoluminescence spectra demonstrate ultraviolet emission peaks which have shift with the increase of Mn ion concentration. The temperature-dependent magnetization (M-T) curves of the ZnO/ $Zn_{1-x}Mn_xO$ thin films were measured by a superconducting quantum interference device (SQUID) magnetometer and the magneto-optical properties were measured by micro-MOKE spectroscopy. The results show the room temperature ferromagnetism of the ZnO/ $Zn_{1-x}Mn_xO$ thin films suggested that the possibility for the application to diluted magnetic semiconductors.

EM-ThP5 The Formation of Stable GeO_2 Oxide on Germanium Epitaxial Layer using the High Pressure Oxidation*, Nakjun Choi,* *J.H. Bae,* Sungkyunkwan University, Republic of Korea

Thermal oxidized of Ge films under high pressure have been investigated to examine the possibility for the gate oxide. Ge oxides were grown either Ge wafers or Ge epitaxial films grown on Si wafer. The temperature range was from 450 °C to 550 °C, and three different pressures such 10, 30, and 50 atm were chosen for a high pressure dry oxidation. The physical property of GeO_2 films were analyzed using the transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy(XPS). Additionally, $Au/GeO_2/Ge$ MOS capacitors were characterized using C-V and I-V measurement. The hysteresis behavior in C-V characteristics and the interface trap density (D_{it}) are significantly reduced through the high pressure oxidation. Consequently, the properties of both GeO_2 film and GeO_2/Ge interface are successfully improved by suppressing GeO volatilization utilizing high pressure.

EM-ThP6 NH_4OH Solution Wet Etching for Silicon Channel Thinning of Junctionless-FET*, Lucas Stucchi-Zucchi,* *A.R. Silva, J.A. Diniz,* University of Campinas, Brazil

Junctionless-FET (JL-FET) devices were fabricated on SOI substrate using NH_4OH solution silicon etching as means to thin the channel substrate. The devices gate dielectric was silicon oxynitride grown using O_2/N_2 ECR (Electron-Cyclotron-Resonance) plasma, and its gate metal was TiN defined through lift-off and deposited using reactive sputtering. The electric contacts were fabricated with sputtered aluminum defined through lift-off and annealed on a conventional oven. Samples were characterized during the fabrication processes using optical microscopy and scanning electron microscopy (SEM). The device electrical performance was measured using a probestation and then cross-section SEM images were extracted using Ga+ Focused Ion Beam milling.

The final channel thickness was 65nm measured in the cross-section images, which also showed the angled sidewalls characteristic of the NH_4OH solution wet etching. The channel dopant concentration was estimated at approximately 10^{17} atoms/cm^3 through Pseudo-MOS electrical measurements, this was the doping concentration that was planned according to the simulation steps to ensure transistor behavior by sacrificing electrical contact quality. Electrical measurements showed transistor behavior and low leakage currents, despite the negative threshold voltage and poor electrical contacts, which distorted the I-V measurements due to their Schottky-like behavior. These results are as expected due to the measured channel thickness and the estimated channel dopant concentration and point favorably towards the silicon etching in NH_4OH solution being a viable technique to fabricate JL-FET devices.

In the future, Atomic Force Microscopy (AFM) measurements will be used to measure the surface roughness after the silicon wet etching in NH_4OH solution. With a more accurate etching rate, new samples will be fabricated with thinner channel thicknesses and higher dopant concentration. The enhanced fabrication process is expected to result in JL-FET devices that rival the performance of state-of-the-art MOSFET devices.

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EM-ThP7 Fabrication of Highly-Efficient Nanoscale Multilayered Thin-Film Thermoelectric Devices*, **Alandria Henderson**, J. Kimbrough, Z. Duncan, K. Davis, M. Howard, J. Elike, T. Wimbley, M. Glenn, Z. Xiao,* Alabama A&M University

We report the growth of nanoscale multilayered thermoelectric thin films and fabrication of integrated thermoelectric devices for high-efficiency energy conversion and solid-state cooling. Nanoscale multilayered thin films such as Sb/Sb_2Te_3 and Te/Bi_2Te_3 thin films were grown using the e-beam evaporation. Integrated thermoelectric devices were fabricated with the nanoscale multilayered thin films using the clean room-based microfabrication techniques such as UV lithography. X-ray diffraction and reflection and high-resolution tunneling electron micrograph (HR-TEM) were used to analyzed the e-beam-grown nanoscale multilayered thin films. SEM was used to image and analyze the fabricated devices. The thermoelectric characteristics of the fabricated devices were measured and analyzed, and highly-efficient thermoelectric thin-film materials and integrated devices will be demonstrated and reported.

EM-ThP9 Control of Randomness in Microsphere-Based Photonic Crystals Assembled by Langmuir-Blodgett Process*, **Sarun Atiganyanun**, O.K. Abudayyeh, S.M. Han, S.E. Han,* University of New Mexico

Photonic structures in biological systems typically exhibit an appreciable degree of disorder within their periodic structures. Such disorder contributes to unique optical properties but has not been fully understood. Towards the goal of improving this understanding, we have investigated Langmuir-Blodgett (LB) assembly of silica microspheres to controllably introduce randomness to photonic structures. We theoretically modeled the LB assembly process and determined a condition for surface pressure and substrate pulling speed that results in maximum structural order. For each surface pressure, there is an optimum pulling speed, and vice versa. Photonic structures fabricated at various conditions were characterized by scanning electron microscopy and light scattering analysis, which confirms the modeled optimum condition. However, along the trajectory defined by the optimum condition, the structural order decreases moderately as the pulling speed increases. This moderate decrease in structural order would be useful for controlled introduction of randomness into the periodic structures. Departing from the trajectory, our experiment reveals that a small change in pulling speed at a given surface pressure can significantly disrupt the structural order. According to these observations, mechanism of forming structural order in LB assembly is proposed. Additionally we also find that, for multilayer LB assembly at a fixed pulling speed, the surface pressure should increase as the number of layers increases to achieve maximum structural order. In summary, this work quantitatively presents the optimum trajectories for n^{th} layer assembly relating surface pressure and pulling speed.

EM-ThP10 Incorporation of Ferroelectric HfO_2 into Magnetoelectric Random-Access Memory (MeRAM) Devices*, K. Fitzell, **Jeffrey Chang**, A. Acosta, H. Ma, X. Li, K.L. Wang, J.P. Chang,* University of California, Los Angeles

In contrast to manipulating magnetization with applied current, using an applied electric field can significantly reduce the required energy and result in less heat generation, leading to increased ene rgy density. This can be accomplished using the voltage-controlled magnetic anisotropy (VCMA) effect, which forms the basis of next-generation magnetoelectric MRAM devices. Specifically, applying an electric field across a CoFeB/MgO interface can decrease the perpendicular magnetic anisotropy field as a result of the altered electron density at the interface, thus destabilizing the magnetization state and allowing for its efficient and deterministic reorientation with a small applied magnetic field. This op eration principle stands in contrast to that of STT-RAM, which uses upwards of 100 fJ to write a single bit (300,000 times more energy than the actual energy barrier to switching).

Previous research on CoFeB/oxide interfaces has shown that increasing the dielectric constant of the oxide layer also increases the sensitivity of the interfacial magnetic anisotropy energy to an applied electric field (Kita et al., 2012). Our previous work involving MgO/PZT/MgO composite tunneling barriers showed a 40% increase in the VCMA effect upon addition of PZT to the tunneling barrier. However, the ferroelectric order of PZT is very weak at such small dimensions, and the leakage current and high annealing temperatures required of PZT prevent this technology from being industrially relevant. On the other hand, the orthorhombic phase of HfO_2 has been shown to possess desirable ferroelectric properties even in ultrathin films. In addition, ferroelectric HfO_2 boasts superior compatibility with CMOS technology as well as desirable electrical properties for device integration.

In this work, a method for depositing orthorhombic phase HfO_2 (FE-HfO_2)-based thin films via a radical-enhanced atomic layer deposition process is described. These ferroelectric thin films were subsequently incorporated into the tunneling junctions of CoFeB/MgO-based magnetic tunnel junction in an effort to enhance the VCMA effect and introduce ferroelectric functionality into magnetoelectric random-access memory devices.

EM-ThP11 Extreme Environment Operation of $Al_{0.85}Ga_{0.15}N/Al_{0.7}Ga_{0.3}N$ High Electron Mobility Transistors*, **Patrick Carey**, F.R. Ren,* University of Florida*; A.G. Baca, B. Klein, A.A. Allerman, A.M. Armstrong, E.A. Douglas, R.J. Kaplar,* Sandia National Laboratories*; S.J. Pearton,* University of Florida

$Al_{0.85}Ga_{0.15}N/Al_{0.7}Ga_{0.3}N$ high electron mobility transistors (HEMT) underwent DC characterization across the temperature ranging from room temperature to 500°C. Due to a high Schottky barrier height and low gate leakage current achieved on Al0.85Ga0.15N barrier layer, drain current modulation up to a gate voltage of 10 V was demonstrated at 500°C. The high aluminum content in these devices enables stability at high temperature due to the ultra-wide bandgap of ~ 5.7 eV. Conventional low Al content HEMT devices have previously shown improved elevated temperature operation as compared to their Si or GaAs counterparts, but are unable to operate under extreme temperature tested herein and suffer from high gate leakage current with heating. The drain current on/off ratio of 1011 were obtained with low gate leakage currents. The drain current degraded by ~50% from room temp to 500°C. The subthreshold slope of 80 mV/dec and 230 mV/dec were obtained at room temperature and 500°C, respectively. From the subthreshold slopes, trap densities were calculated to be 2.3×10^{11} cm^{-2} at room temperature and 3.3×10^{12} cm^{-2} at 500°C. These novel devices show great promise for application in the power, space, and defense industry where extreme performance is necessary.

EM-ThP12 Electrical Characterization of the Reduced Effective Schottky Barrier Height by Nanoscale Ge bi-layer of CZTSe Solar Cells*, **Sanghyun Lee**,* Indiana State University

In the past ten years, there have been constant attempts to develop high efficient thin film solar cells, which are cost-effective, environmentally benign, and reliable. The most strongest candidate of emerging alternatives is $Cu_2ZnSn(S,Se)_4$ (or kesterite) solar cells, herein CZT(S,Se). With abundant elements in earth's crust, CZT(S,Se) shows high absorptions coefficient (>10^4 cm^{-1}) and a tunable direct band gap energy, ranging from 1 to 1.4 eV, which makes it an ideal platform for future renewable energy devices . However, the efficiency improvement and understanding of emerging CZT(S,Se) is still in early stage compared to the counterparts such as $Cu(In,Ga)Se_2$ (CIGS) and CdTe. In recent progress, Germanium (Ge) incorporation into CZT(S,Se) solar cells has received extensive attention to deepen the understanding of this types of devices as Ge-alloyed CZT(S,Se) solar cells have demonstrated improvements in device performance. However, several challenges still remain such as a large Voc-deficit, sever heterojunction interface recombination, and a Schottky-type back contact barrier.

The presence of Schottky barrier near back contact limits the hole movement which influences the current-voltage characteristics and deteriorates the Voc-deficit as well. To investigate the impact of this back contact barrier height, we fabricated and characterized a set of CZTSe solar cells by utilizing DC magnetron sputtering by applying ultra thin Ge nanolayers. We investigated the back contact interface between $CZTSe/MoSe_2$ and Mo metal contact in an effort to improve a back contact barrier. By incorporating nanoscale Ge bi-layers below and below the absorber, a barrier height is considerably improved. The results indicate that nanoscale Ge bi-layers improves the back contact barrier height by 27 % as compared to CZTSe:Ge monolayer devices (see a supporting document device A). The back contact improvement is possibly caused underlying Ge nanolayer (<2.5 nm) between the absorber and Mo metal contact. The improvement of the efficiency loss caused by the series resistance component is reduced by 50%, which is attributed to the improved Schottky-type back contact barrier. This allows the improved efficiency up to 8.3% by incorporating nanoscale CZTSe: Ge bi-layers.

EM-ThP13 Optimal Contact Photolithography Techniques For HEMT Substrates using I-line Photoresist*, **Whitney Ingram**, A. Jones, B. Klein, A.G. Baca, A.M. Armstrong, A.A. Allerman, E.A. Douglas,* Sandia National Laboratories

Gallium nitride-based high electron mobility transistors (HEMTs) utilize a variety of substrates, including those that are optically transparent in the visible and ultraviolet wavelength spectrum such as sapphire and silicon carbide(SiC). Compared to silicon substrates, SiC and sapphire substrates can exhibit a distinct set of photolithography patterning challenges such as backscattering (from the underlying chuck and other areas of the substrate) which can influence the critical dimension (CDs), pattern integrity, and pattern resolution. In this study, computational photolithography and rigorous coupled wave guide analysis are used to calculate the optical reflectivity, the transmission and absorption of a multilayered stack comprised of i-line photoresist and an antireflective coating on sapphire substrates with $Al_xGa_{1-x}N$ epitaxial layers (with x ranging from 0 to 1). These simulations are used to target optimal resist and arc thickness, and exposure energy needed to reach the target feature with high fidelity. As a proof of concept, fully resolved patterns down to 0.5 µm are experimentally obtained on sapphire substrates using conventional contact photolithography driven by simulated for optimal conditions. Due to the lack of experimental information on photolithography on optically transparent substrates with ultra-wide bandgap heterostructures, this method can provide relevant insight into determining optimal process window for optically transparent substrates.

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EM-ThP14 High-mobility Helical Tellurium Field Effect Transistors Enabled by Transfer-free, Low-temperature Direct Growth*, **Guanyu Zhou**, R. Addou, Q. Wang, S. Honari, C.R. Cormier, L. Cheng, R. Yue, C.M. Smyth, A. Laturia, J. Kim, W.G. Vandenberghe, M.J. Kim, R.M. Wallace, C.L. Hinkle,* University of Texas at Dallas

The transfer-free direct growth of high performance materials and devices could enable transformative new technologies. Here we report room temperature field-effect hole mobilities as high as 707 $cm^2V^{-1}s^{-1}$, achieved using transfer-free, low-temperature (≤120°C) direct growth of helical tellurium (Te) nanostructure devices on SiO_2/Si. The Te nanostructures exhibit significantly higher device performance than other low-temperature grown semiconductors, and we demonstrate that through careful control of the growth process, high-performance Te can be grown on other technologically relevant substrates including flexible plastics like polyethylene terephthalate (PET) and graphene in addition to amorphous oxides like SiO_2/Si and HfO_2. The morphology of the Te films can be tailored by the growth temperature, and we identify different carrier scattering mechanisms for films with different morphologies. The transfer-free direct growth of high-mobility Te devices could enable major technological breakthroughs, as the low-temperature growth and fabrication is compatible with the severe thermal budget constraints of emerging applications. For example, the vertical integration of novel devices atop a silicon complementary metal oxide semiconductor (CMOS) platform (thermal budget <450 °C) has been theoretically shown to provide a 10x systems level performance improvement, while flexible and wearable electronics (thermal budget <200 °C) could revolutionize defense and medical applications.

EM-ThP18 100 keV Proton Irradiation Effects on AlGaN/GaN Epistructures*, **Min Khanal**, S. Uprety, K. Yapabandara, V. Mirkhani, S. Wang, B. Schoeneck, T. Isaacs-Smith, A. Ahyi, M.J. Bozack, M. Park,* Auburn University

The electronics that are used in spacecraft are subject to space radiation hazards. The space radiation environment includes trapped electrons and protons of the Van Allen radiation belts, and non-trapped transient solar and galactic cosmic rays and solar flare particles. The protons with the cut-off energy of 100 keV are present above the upstream of the Earth's bow shock. Since gallium nitride and its alloys are proven to be relatively radiation tolerant, these materials are considered as promising candidates for space electronic applications. Therefore, it is consequential to study the effect of 100 keV protons on the AlGaN/GaN HEMTs if the devices are to be used for space applications. In this research, the effect of 100 keV protons with the fluences 1×10^{10}, 1×10^{12}, and 1×10^{14} cm^{-2} on materials/device characteristics of AlGaN/GaN HEMTs constructed on Si wafers were studied by means of optical and electrical characterization. The electrical characteristics of the devices were analyzed by using conventional transistor I-V and C-V measurements in order to relate the material's fundamental properties to the device performance. The slight degradation on the electrical characteristics and the shift in the threshold voltage was observed in the irradiated samples. The crystal quality of the epilayer was examined *via* micro-Raman spectroscopy and no substantial degradation in the crystal quality was observed.The possible introduction and/or the alternation of the defects were probed using the photoluminescence (PL) spectroscopy and spectroscopic photocurrent-voltage techniques. The surface morphology of the samples was studied by atomic force microscopy (AFM) and scanning electron microscopy (SEM), and a slight increase in the surface roughness was observed. The surface analysis was performed using X-ray photoelectron spectroscopy, and the surface elemental composition was not altered after irradiation. It is concluded that the crystal quality of the AlGaN/GaN HEMT layers and the electrical characteristics of the AlGaN/GaN HEMTs were not severely degraded in spite of the exposure to a high fluence of protons with the energy 100 keV.

EM-ThP19 Properties of WSe_2 Thin Films Grown by Molecular Beam Epitaxy*, P. Litwin, K.M. Freedy, T. Zhu, M. Zebarjadi, **Stephen McDonnell**,* University of Virginia

The synthesis of high quality transition metal dichalcogenide (TMD) films is of significant interest for potential applications in nanoelectronic and thermoelectric devices. Molecular beam epitaxy (MBE) is a promising route, providing fine control over growth conditions. To further understand the growth conditions on film quality, we study the effect of processing conditions on the resultant material quality. MBE is used to synthesize bilayer $WSe_2$and it is shown using in-vacuo x-ray photoelectron spectroscopy (XPS) that the process conditions can directly influence the resultant chemistry and electronic structure. Specifically, we show that the initial nucleation conditions are critical to achieving repeatable and high-quality WSe_2. Our combination of MBE and in-situ XPS studies show that WSe_2chemistry can be controlled through processing conditions. We also use ex-situ characterization to determine properties such as cross-plane resistance and Seebeck coefficient. It is shown that Ni and Au contacts result in negative and positive Seeback coefficients respectively. Furthermore, Ni contacts are found to degrade over time.Presented will be our results showing the process control of WSe_2chemistry. Also shown will be the impact of these changes on device relevant properties, such as resistance and Seebeck coefficient.

EM-ThP20 Effects of O_2 Partial Pressure on Ga_2O_3 Thin-films*, **Seth King**,* University of Wisconsin - La Crosse

Gallium oxide (Ga2O3) has recently become recently become a material of great interest due as it is a stable, wide bandgap oxide which is capable of being used as a transparent conducting oxide or dielectric layer in the next generation of electronic devices [2]. While the majority of work has focused on single crystal materials, few results exist regarding the growth and nucleation of polycrystalline Ga2O3 materials [2,3].

The present study utilizes spectroscopic ellipsometery, x-ray diffraction, and four-point resistivity measurements to investigate how the physical properties of Ga2O3 thin-films may be altered by changing the partial pressure of O2 during reactive RF sputter deposition. The results will yield important information regarding how material properties are related to deposition conditions using an industrially applicable fabrication process.

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Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room Hall B - Session HC-ThP

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic Poster Session

HC-ThP2 *In situ* Infrared and Catalytic Reaction Studies of Active Sites on Pt Nanoparticles Supported on Nanosponge Oxides under CO oxidation*,* ***Sunyoung Oh,*** Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea*; C.H. Jung,* Institute for Basic Science (IBS), Republic of Korea*; H. Ha,* Chungnam National University, Republic of Korea*; C. Jo,* Institute for Basic Science (IBS), Republic of Korea*; S.Y. Moon, Y.K. Kim,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea*; W.H. Doh,* Institute for Basic Science (IBS), Republic of Korea*; H.Y. Kim,* Chungnam National University, Republic of Korea*; R. Ryoo, J.Y. Park,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Platinum-based heterogeneous catalysts are mostly used in various commercial chemical processes because of their highly catalytic activity influenced by the metal-oxide interaction. To design the rational catalysts with high performance, it is crucial to understand the reaction pathway. Here, Pt nanoparticles supported on nanosponge oxides such as TiO_2 and SnO_2 with advantage of high surface area, thermal stability, and quite high interfacial sites were synthesized and utilized in CO oxidation reaction to prove the interaction of the metal and support. CO oxidation results show high activity for Pt supported on TiO_2 nanosponge catalyst, which is associated to the O_2 dissociation at the Pt/TiO_2 perimeter sites. *In situ* infrared (IR) spectroscopic observation indicates that oxygen molecule bond is activated at the Pt/TiO_2 interface by neighbor CO molecules on the Pt surface. The computational calculations for proposed reaction mechanism for O_2 activation at Pt/TiO_2 interface are consistent with experiment results. In contrast, we directly observe that absence of adsorbed CO on Pt surface for Pt/SnO_2 catalyst by using IR because the Pt surface as active site was covered with a shell of tin oxide after hydrogen pre-treatment. These results allow us to obtain the insight into the nature of metal-support interface between Pt and nanosponge oxide supports and reaction pathways of CO oxidation for Pt-based supported catalysts.

HC-ThP3 Activity of Bimetallic Pt-Re Surfaces and Influence of the Support for the Water-Gas Shift Reaction*,* ***Amy Brandt***[1]*, T.D. Maddumapatabandi, D. Shakya, S. Farzandh, D.A. Chen,* University of South Carolina

Bimetallic Pt-Re clusters are systematically investigated on model supports in order to understand the effects of metal-metal interactions and metal-support interactions on cluster formation and catalytic activity for clean hydrogen production via the water-gas shift (WGS) reaction. Bimetallic catalysts have exhibited unique characteristics different from their single metal constituents, and interactions with the support are believed to have an influence on the chemistry taking place at the interface. Pure and bimetallic Pt-Re surfaces were prepared in ultrahigh vacuum (UHV) by vapor-deposition on model supports of TiO_2(110), Pt(111), and highly oriented pyrolytic graphite (HOPG). WGS activity was studied in a UHV-coupled microreactor operating at a temperature of 160 °C and pressures of ~1 atm. On the TiO_2 support, bimetallic clusters consisting of Pt at the surface and Re residing subsurface were found to have the highest activity for the WGS reaction, with turnover frequencies (TOF) nearly twice as high as monometallic Pt on TiO_2. The TOF on the Pt single crystal was lower than Pt clusters supported by TiO_2. A Pt-Re alloy with pure Pt at the surface and Re residing subsurface showed enhanced activity over pure Pt(111). Pt clusters deposited on TiO_2 were investigated by scanning tunneling microscopy and found to have an increasing number of perimeter atoms compared to total atoms at decreasing Pt coverages. WGS experiments revealed a trend of increasing TOF for Pt coverages with increasing perimeter atom percentages, suggesting the Pt/TiO_2 interfacial sites contribute to WGS activity. An alternative support of HOPG confirmed that Pt clusters on TiO_2 have a greater TOF than Pt clusters on HOPG for the WGS reaction. In contrast to bimetallic Pt-Re clusters on TiO_2, Pt-Re clusters on HOPG consisted of higher concentrations of Re at the surface, leading to lower TOFs for Pt-Re clusters on HOPG than the monometallic Pt on HOPG surface.

HC-ThP4 In-Operando Photoluminescence Imaging of a Single-Layer Molybdenum Disulfide Catalyst*,* ***Koichi Yamaguchi,*** University of California - Riverside*; S. Naghibi, W. Coley, L. Bartels,* University of California, Riverside

MoS_2 is the key industrial catalyst for hydrodesulfurization (HDS) of crude oil. Atomistic investigation of the HDS reaction is hampered by the elevated pressures and temperatures required for HDS. There is close correlation between the current industrial catalyst material and model single-layer MoS_2 flakes. We developed a new experimental approach that relies on strong photoluminescence (PL) of monolayer MoS_2 that we grow efficiently on an inert SiO_2 substrate. We find that wide-field PL imaging is possible even under near in-operando condition and can serve as a reporter of the chemical state and spatial variation of the catalyst material. Our experiments proceed under up to 1atm of hydrogen, any volatile thiol, and at temperatures of up to 400 °C. Spatially resolved images allow us to distinguish between reactions at island edges and the basal plane; desulfurization and binding of organic species to the catalyst are reported as bleaching of the photoluminescence. Concomitant mass spectrometric analysis allows us to correlate the variation in the island PL with different reaction regimes.

HC-ThP6 Comparative Reactivity of Oxide and Metallic Phases on Rh(111)*, R.G. Farber, M.E. Turano, W. Walkosz,* ***Christopher Smith****, D.R. Killelea,* Loyola University Chicago

Recently, the understanding of the role of surface oxides in catalytic activity has changed. Instead of being thought of as poisons, similar to bulk oxides, they are now believed to be effective promoters of selective catalysis. We have chosen to study oxidation on Rh(111) as a model system; Rh effectively promotes oxidation reactions and is a benchmark system for models of heterogeneously catalyzed chemistry. Using atomic oxygen (AO) as an oxidizing agent, high coverage oxygen adlayers and oxides can be formed under ultra-high vacuum (UHV) conditions. Careful control of the AO exposure parameters allowed for the selective growth of the RhO_2surface oxide, surface adsorbed oxygen, and subsurface oxygen. Furthermore, formation of the RhO_2surface oxide was shown to rely not only on the presence of defects, as evident by the selective growth along step edges (Figure 1), but also on high concentrations of oxygen absorbed below the surface of the metal.

Utilizing our surface preparation techniques to carefully prepare specific oxidized Rh(111) surfaces, we use carbon monoxide (CO) as a probe molecule to track surface structure specific reactivity via CO oxidation. Exposing $RhO_2$to CO, TPD and STM are employed to gather information on CO_2production, residual O_2population, and surface structure evolution during CO oxidation reactions. In order to determine the actual reaction mechanism of CO oxidation on oxidized Rh(111), STM is needed to provide atomic scale resolution of the active surface adsorbates during the reaction progression, as shown in Figure 1. By combining spatially resolved structural information with CO_2production and oxygen consumption, we will be able to identify which oxidic species and surface sites contribute to CO oxidation. This information will help in determining the exact reaction mechanism occurring during CO oxidation over an oxidized Rh surface.

HC-ThP7 Hybrid Adsorbent Catalyst for Siloxane Removal: Fe-BEA Zeolites*,* ***Alba Cabrera-Codony,*** University of Girona, Spain*; E. Santos-Clotas, J. Martin,* University of Girona

Different types of both natural and synthetic zeolites, covering a wide range of physical and chemical properties, were evaluated as adsorbents/catalyst for siloxane removal in lab-scale gas phase adsorption tests of octamethylcyclotetrasiloxane (D4). After bed exhaustion, wet oxidation processes were used for the regeneration of the spent zeolite samples, including ozonation and Fenton-like treatment of the Fe-amended zeolites using hydrogen peroxide. New adsorption tests were performed after theses AOP-driven regeneration processes.

The results on the uptake of gaseous D4 by various zeolites led to the conclusion that BEA type materials presented the highest catalytic activity for the siloxane ring-opening and formation of α -ω -silanediols due to the high content of Bronsted and Lewis acidic sites. Those silanediols formed on the BEA surface were detached from the catalytic acidic sites when water was available, and were narrow enough to diffuse into the channels, hence enhancing the removal efficiency for D4.

The water soluble α -ω -silanediols formed by the catalytic activity of the iron exchanged Fe-BEA type zeolites during D4 adsorption were easily removed by wet regeneration treatment with water, however, the regeneration was incomplete, i.e. the adsorption capacity was partially recovered. Adding H_2O_2 in a heterogeneous Fenton-like regeneration

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

treatment led to a complete recovery of the adsorption capacity of the Fe-zeolites samples.

However, on successive adsorption/regeneration cycles, the recyclability of the Fe-zeolites catalysts was hampered by the accumulation of carbonaceous materials on the material surface, which caused a loss of the catalytic activity, affecting both the adsorption and the regeneration stages.

Bronsted acidic sites (BAS) and Lewis acidic sites (LAS) promoted the D4 transformation into silanediols, as shown in Figure 1, which was the fundamental step that ruled the D4 uptake on the gas adsorption process. At the same time, the iron exchanged in Fe-BEA type zeolites promoted the catalytic activity towards Fenton-like reactions for the regeneration of the exhausted materials.

Advanced Ion Microscopy Focus Topic
Room Hall B - Session HI-ThP

Advanced Ion Microscopy Poster Session

HI-ThP1 He+ and Ne+ Ion Beam Resolution Dependency on Beam Energy*, Waqas Ali,* Intel Corporation, USA*; S. Tan,* Intel Corporation*; R.M. Hallstein, R.H. Livengood,* Intel Corporation, USA

For several decades, Gallium (Ga+) remained an ion species of choice for circuit edit (CE) applications due to its excellent micro and nanomachining capabilities. But due to continuous device scaling, now it is becoming highly challenging to fulfill all the needs of CE with Ga+ based focused ion beam (FIB) tools. Recently Neon gas field ionization source (GFIS) has emerged as one of the most viable solutions to supplement CE requirements where a Ga+ FIB falls behind [1]. A lot of effort has gone into the beam characterization of the Neon (Ne+) and Helium (He+) beams of Orion NanoFab that is the first GFIS based commercial tool. In this paper, we present our results on resolution characterization of He+ and Ne+ beams as a function of beam energy.

He+ beam resolution characterization was done at 10, 20 and 30 kV beam energies whereas Ne+ beam resolution was characterized at 10 and 25 kV. The test was conducted on CVD graphene on TEM grid and ImageJ was used for image analysis. The lateral resolution for Helium was 0.54 ± 0.07 nm at 30 kV beam energy whereas for Neon the resolution was 2.45 ± 0.46 nm at 25 kV beam energy both with 100 fA beam currents. The unparalleled resolution specs. of Ne+ and He+ ion beams have made them attractive not only for CE but for many other applications like high resolution imaging for fault isolation, failure analysis, EUV mask repair, lithography, graphene patterning, plasmonics and biological imaging etc. [2].

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HI-ThP2 *Focused Cs Ion Beam-Induced Deposition and Gas Assisted Etch Characterization Results for 10nm Circuit Edit Applications, Roy Hallstein,* *R.H. Livengood, M.P. Ly,* Intel Corporation, USA*; Y. Greenzweig, Y. Drezner,* Intel Corporation, Israel*; B.J. Knuffman, A.V. Steele, A.B.J. Knuffman,* zeroK NanoTech

Focused Ion Beam Gas Assisted Etch (GAE) and Ion Beam Induced Deposition (IBID) are used extensively in Circuit Edit nanomachining. Historically the Gallium Focused Ion Beam (FIB) has been the primary ion source technology for Circuit Edit applications. [1, 2] More recently, the neon and nitrogen (N_2) gas field ion sources (GFIS) have also been introduced to enable very small, high precision nanomachining for circuit rewiring and mask defect repairs respectively. [3, 4, 5] Other emerging ion source technologies are the so-called ‘cold ion’ sources, which ionize atoms that have been laser-cooled to micro-kelvin temperatures. These sources have been shown to have high brightness and low energy spread, enabling small focal spot sizes. [6] Two such emerging ‘cold’ sources that produce cesium ion beams are under development by zeroK NanoTech Corporation and Tescan Orsay Holding. [7, 8]

As part of the due diligence to identify breakthrough ion beam technologies to keep pace with nanomachining applications scaling requirements, we have completed preliminary analysis of the attributes of cesium for Circuit Edit applications. In this paper, Proof of Concept 10nm Circuit Edit results using the zeroK Nanotech Cesium ion beam-based GAE and IBID will be presented. Preliminary results include GAE chemical etching of semiconductor materials and IBID results for dielectric and metal depositions. Finally, preliminary electrical test results of proof of concept Circuits Edits on 10nm process node will be presented.

Magnetic Interfaces and Nanostructures Division
Room Hall B - Session MI-ThP

Magnetic Interfaces and Nanostructures Division Poster Session

MI-ThP1 Synthesis and Size Dependent Magnetic Properties of Iron Oxide Nanoparticles*, Jeremy Winsett,* *A. Moilanen, S. Neupane,* Middle Tennessee State University

Fe_2O_3, and Fe_3O_4 nanoparticles were synthesized by means of a simple hydrothermal procedure. The experimental parameters were varied to produce nanoparticles of different sizes and morphologies. Variation in growth temperature, duration, precursor concentration, and surfactants will influence the geometry and hence the magnetic properties of nanoparticles. Scanning electron microscopy, transmission emission microscopy and X-ray diffraction were used to characterize as-synthesized magnetic nanoparticles. Saturation magnetization and hysteresis measurement were determined using a vibrating sample magnetometer. Nanoparticles exhibiting size-dependent magnetic properties can find applications in targeted drug delivery, magnetic separation, contrast enhancement in magnetic imaging and others.

MEMS and NEMS Group
Room Hall B - Session MN-ThP

MEMS and NEMS Group Poster Session

MN-ThP1 The Ni-Co Micro-porous Array with High Dimensional Accuracy Control by Electroforming Process*, YuHsin Lin,* *H.J. Wen,* ITRC,NARL, Taiwan, Republic of China*; C.J. Tsia,* NCTU, Taiwan, Republic of China*; M.-K. Wang, N.N. Chu, C.C. Chen, C.-N. Hsiao,* ITRC,NARL, Taiwan, Republic of China

In this project, the Ni-Co micro-porous array membrane for ultra-high sensitivity gas detector for nano particle distribution measurement is developed for cascade impactor application. The thick film lithography and electroforming technologies have been integrated, here. The dimension of micro-porous can be precisely controlled and reproducible. Finally, the micro-porous metal film will be integrated with base structure by laser welding technology. The component is used for cascade impactor equipment.

The fabrication process of Ni-Co micro-porous array membrane is used MEMS process. Here, the 6 inch silicon wafer as a substrate is used. The Cr/Au with 30/200nm thickness as a seedlayer is made by Sputter. The gold has good electrical conductivity to get well Ni-Co thickness uniformity at electroforming process. The AZ6112 photoresist is patterned on the seedlayer by lithography. The Cr/Au is etched to define a circle pattern. Then the thick photoresist SU8 pillar with 150μm thickness is fabricated at the center of the circle seedlayer pattern. The diameter of SU8 at the bottom is used to control the final diameter of Ni-Co porous. The Ni-Co membrane with 130μm thickness has been fabricated by electroforming process. Finally, the SU8 pillar is removed and the Ni-Co porous membrane is peel off from substrate. The Ni-Co micro-porous array membrane with good hole’s dimension control have successful fabricated.

***Keywords*: Micro-porous, Electroforming, cascade impactor**

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MN-ThP2 Reactive Etching of AlGaN using BCl_3 and Ar/BCl_3*, Meng-Kun Wang,* *Y.-H. Lin, C.-N. Hsiao, C.C. Chen, J.S. Su, N.C. Chu, C.-T. Lee,* ITRC,NARL, Taiwan, Republic of China

In this paper, we study the self- limited reaction of Ar/BCl_3 and AlGaN. We performed AlGaN surface oxidation reaction with oxygen ions before

Ar/BCl_3 etching on the AlGaN surface, and used the same power of inductively coupled plasma (ICP), the same working pressure, and the same The etching time was compared to the difference in etching rate of AlGaN between Ar/BCl_3 and BCl_3. And using Atomic force microscopy (AFM) and scanning electron microscopy (SEM) to observe the change and morphology of the surface roughness after etching. The results show that the mixed gas of Ar/BCl_3 has a faster etching rate, the etching rate is about 4.79 nm/min, and the etching rate of BCl_3 gas is slow, and the etching rate is about 0.90 nm/min.

MN-ThP4 III-V_Si Wafer Bonding using Silicon Oxide Interlayer*, **WoongSun Lim**, S.H. Jung,* Korea Advanced Nano Fab Center, Republic of Korea*; S.Y. Hwang,* Korea Advancnced Nano Fab Center, Republic of Korea*; G.Y. Yeom,* Sungkyunkwan University, Republic of Korea

In recently, the interests to integrate III–V based materials with Si can be divided into various application using the material advantages of combining III–V with Si. Therefore, Si wafer to III-V material wafer bonds were performed at low temperatures under 250 °C. The advantage of the low temperatures of these bonds was that wafers with common integrated circuit metals could withstand this temperature without degradation. Also, it is essential to study that low temperature bonding for heterogeneous wafers, because the higher temperature bonding may induce cracks, defects, bowing, and destruction by different thermal expansion coefficients of the heterogeneous wafers.

In this paper, we have investigated low-temperature direct bonding (<250°C) of SiO2 by the surface activation method in plasma. In the method, Oxyzen plasma treatment is used to make a clean surface which has strong bonding ability.The strength of Si oxide to Si oxide bonding prepared at room temperature by the method is equivalent to the bulk strength. Therefore, heating and pressure were applied to the wafers 20 minutes. Si oxide surfaces did not prove to bond spontaneously at room temperature and the bond-strength started to increase only after annealing at about 200°C.

A field emission scanning electron microscopy (FE-SEM) was used to determine the excellent bonding quality of the interface of wafer to wafer bonding. Silicon oxide surface roughness was examined using atomic force microscopy(AFM), respectively. After bonding, the bonded interfaces were evaluated using infrared transmission imaging.

MN-ThP5 Flexible Nanocomposite Sensors for Biomedical and Energy Harvesting Applications*, A.K. Batra, **Bir Bohara**,* Alabama A&M University*; R. Currie,* NASA

Recently, an increase in demand for sensors for biomedical and ambient energy harvesting applications has led to the development of new hypersensitive smart materials. Biomedical sensors need to be able to be both lightweight, flexible and demonstrate high piezoresistive resolution. In order to meet the pressure sensor requirements for the next generation of prosthetics, efforts were made to develop and characterize multifunctional smart flexible nanocomposite films. The developed improved films could be used for both biomedical and energy harvesting applications. Nanocomposites PVDF and P(VDF-TrFE) film-sensors were fabricated via embedding smart nanocomposites particles along with a variety of carbon nano-particles via the modified solution casting method. The fabrication methods involved in this study aimed at improving the sensitivity of sensors while maintaining flexibility and cost efficiency. The fabricated films were characterized by infrared and dielectric spectroscopy; performance of the sensors was determined via customized strain measurement and energy harvester testing system. Results obtained will be described along with unique features of system developed for performance determination. [This work is funded by NSF-HRD-1546965 grant.]

MN-ThP6 Comparative Studies of Electrical Behavior of PLZT Thin Film Capacitors using Coplanar and Interplanar Configurations*, **Vaishali Batra**, R. Paul, S. Kotru,* The University of Alabama

Lanthanum doped lead zirconate titanate (PLZT) is an interesting ferroelectric material which finds applications in optical MEMS & modulators/transducers, and smart sensors. Recent studies revealing the existence of bulk photovoltaic (PV) effect in this material thereby eliminating the need of fabricating a p-n junction, has generated curiosity among research community to explore this material for future energy/photo sensing applications. Various approaches are being explored to improve the PV output obtained from these devices.

In this work, capacitors with two electrode configurations viz. coplanar and interplanar were used to measure electrical properties. The capacitors were fabricated using thin films of $Pb_{0.95}La_{0.05}Zr_{0.54}Ti_{0.46}O_3$ (PLZT) and top and bottom electrodes of conducting materials. A chemical solution deposition method was used to prepare the films. The capacitance-voltage and polarization-voltage measurements demonstrated that the coplanar configuration shows higher capacitance, lower polarization, and higher coercive voltage as compared to the interplanar configuration. Further, the capacitors with coplanar configuration also demonstrated higher PV parameters, such as short circuit current density (J_{sc}) and open circuit voltage (V_{oc}). As an example, J_{sc} of 1.86 $\mu A/cm^2$ and V_{oc} of -1.1 V were obtained using coplanar configuration with Au electrodes for unpoled devices. Poling showed an improvement in PV parameters for both the coplanar and interplanar configurations, with higher values obtained from the coplanar configuration. After poling, J_{sc} of 1.32 $\mu A/cm^2$ and V_{oc} of -0.93 V for interplanar configuration, and J_{sc} of 2.04 $\mu A/cm^2$ and V_{oc} of -2.01 V for coplanar configuration were obtained. These results suggest that coplanar configuration is better for measuring the PV properties of PLZT thin film based capacitor structures.

Nanometer-scale Science and Technology Division
Room Hall B - Session NS-ThP

Nanometer-scale Science and Technology Division Poster Session

NS-ThP1 Intermolecular Interactions in Self-Assembled Monolayers on Metal Surfaces Characterized by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy*, J. Schultz, P. Whiteman, **Nan Jiang**,* University of Illinois at Chicago

In order to fully characterize molecular assemblies at the single molecular scale, advanced analytical surface techniques have to be employed. We carried out scanning tunneling microscopy (STM) experiments on two molecules (N-N'-bis(2,6-diisopropylphenyl)-perylene-3,4:9,10-bis(dicarboximide) (PDI) and subphthalocyanine (SubPc)), which are both self-assembled on noble metal substrates. The STM experiments were complemented by tip-enhanced Raman spectroscopy (TERS), surface-enhanced Raman spectroscopy (SERS) and density functional theory (DFT) calculations. In particular, we have interrogated the lifting of an accidental vibrational degeneracy of a mode of PDI on Ag(111) and Ag(100) surfaces, with the most strongly perturbed mode being that associated with the largest vibrational amplitude on the periphery of the molecule. In the other hand, the alignment between expeimental TERS of SubPc on surface and DFT calculated Raman spectrum of gas phase SubPc was quite good, which indicates that the interaction between SubPc molecules in the monlolayer is very weak. New two-dimensional molecular superstructures were discovered to consist of several distinct molecular binding configurations. Both TERS and SERS experiments of SubPc yielded nearly identical vibrational spectra for both binding configurations, consistent with their small adsorption energies (<0.2 eV) as calculated by DFT. Our results demonstrate the necessity of advanced Raman techniques such as TERS when precisely probing molecule-molecule and molecule-substrate interactions.

NS-ThP2 Nanoscale Detection of Surface Plasmon-driven Hot Electron Flux on Au/TiO_2 Nanodiodes with Atomic Force Microscopy*, **Hyunhwa Lee**,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea*; H. Lee,* Institute for Basic Science (IBS), Republic of Korea*; J.Y. Park,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Electrons with high kinetic energy (1-3 eV) can be generated in metals during surface reaction processes. These energetic electrons are called “hot electrons”. A way to detect these hot electrons is by using metal-semiconductor Schottky diode. It was proposed that enhanced light absorption with localized surface plasmon resonance results in amplified hot electron generation by utilizing Au/TiO_2 Schottky diodes. In this scheme, the surface morphology of the metal thin film was modified to a connected gold island structure that exhibits surface plasmons.[1,2]

To probe the enhanced hot electron flows by surface plasmon, we fabricated patterned Au islands on TiO_2 diodes using e-beam evaporator, [3] and measured the local photocurrent with the conductive probe atomic force microscopy under back illumination of the light. The gold pattern has triangle shape with the length of the hypotenuse of 150 nm and the thickness of 20 nm. We found that the photocurrent depends on the wavelength of laser, and the bias between Au and TiO_2. The photocurrent measured at the edge of the Au islands was higher than that on the flat area of Au islands. The result indicates the localized surface plasmon resonance leads to enhancement of hot electron flux.

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NS-ThP3 Surface Functionalization of 2D Mo_2C*, **Yang Zeng**, P.H. McBreen, T. Zhang,* Laval University, Canada

A preliminary study of the surface reactivity of 2D -α-Mo_2C crystallites grown on a copper foil was performed using X-ray photoelectron spectroscopy. Different sample preparation protocols for the as-received materials were explored in order to remove hydrocarbon surface contamination. Annealing in vacuum and in argon led to the formation of graphitic layers while annealing in O_2 lead to almost complete disappearance of the Mo signal. Gentle argon ion sputtering proved effective at removing the hydrocarbon contamination to reveal pristine molybdenum carbide. XPS spectra were recorded following the exposure of the prepared sample at room temperature to furfural. The results are commented on in relation to deoxygenation and olefin metathesis surface chemistry.

NS-ThP4 a-Si:H Spacer Lithography Using Different Mandrels (Al, SiN$_x$ and Photoresist) and Etching Processes (RIE, ECR and ICP)*, **Andressa Rosa**, J.A. Diniz,* UNICAMP, Brazil

Semiconductors nanowires are essential for obtaining present and future electronic devices (transistors) and integrated circuits (microprocessors), which require technologies with dimensions smaller than 50 nm and 10 nm, respectively[1,2]. In this context, Spacer Lithography (SL) or Self- Aligned Double Patterning (SADP) methods for the definition of silicon nanowires (SiNW$_s$), for sub-150 nm width dimensions, were developed. These methods are based on: i) hydrogenated amorphous silicon (a-Si:H) spacers (two thickness values of 60 nm and 150 nm) deposited by ECR-CVD (Electron Cyclotron Resonance (ECR) - Chemical Vapor Deposition (CVD)) at room temperature; ii) three different types of mandrels, aluminum – Al, deposited by sputtering;3 silicon nitride – SiNx , obtained by ECR-CVD; and photoresist, deposited by spinner; and iii) three different etching processes (RIE (Rective Ion Etching), ECR and ICP (Inductively Coupled Plasma). Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to obtain the SiNW widths and the shapes of tridimensional (3D) structures as shown a Figure 1. The Table 1 shows the results of the SiNW width values extracted from SEM images and confirmed by AFM analyses, in related to a-Si:H thickness (60 nm or 150 nm), mandrel materials (Al, SiNx or Photoresist) and etching processes (RIE, ECR or ICP). Furthermore, it is presented the comparison between the original a-Si:H thickness, after deposition and before etching process, and the SiNW width, after the etching, to detect if the lateral anisotropic etching of a-Si:H has occurred (or not), to obtain SiNW less wide than expected. From the results, it can be conclude that our method for the formation of semiconductors nanowires sub-150 nm wide is effective and feasible for 3D devices prototyping. Besides that, RIE and ECR processes present lateral etching, obtaining SiNWs with wide less that the a-Si:H spacer thickness.[3] This result is interesting for the nanostructure formation without the traditional methods (e.g., EBL or 193i).[2] It is important to notice that, the ICP process enable the SiNWs formation with width similar to the a-Si:H spacer, indicating that process is anisotropic.

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NS-ThP6 Fabrication of Carbon Nanotube-Based Electronic Devices with the Dielectrophoresis Method*, **Joevonte Kimbrough**, S. Chance, B. Whitaker, Z. Duncan, K. Davis, A. Henderson, Q. Yuan, Z. Xiao,* Alabama A&M University

We report the deposition and alignment of semiconducting carbon nanotubes with the alternating electric field-directed dielectrophoresis (DEP) method and the fabrication of carbon nanotube-based electronic devices with the DEP-aligned semiconducting carbon nanotubes (CNTs). Semiconducting carbon nanotubes, which were dispersed ultrasonically in solutions, were deposited and aligned onto a pair of gold electrodes using the dielectrophoresis method. The DEP-aligned tubes were further fabricated into carbon nanotube field-transistors (CNTFETs) and CNTFET-based electronic devices such as CNT-based inverters and ring oscillators using the microfabrication techniques. The aligned carbon nanotubes and fabricated devices were imaged using the scanning electron microscope (SEM), and the electrical properties were measured from the fabricated devices using the semiconductor analyzer. The semiconducting CNTs achieved higher yield in the device fabrication, and the fabricated devices demonstrated excellent electrical properties.

NS-ThP7 Fabrication and Electrical Characterization of a Flagella-Scaffolded Metallic Nanocluster Network*, **Marko Chavez**, P.J. Edwards, M.Y. El-Naggar, V.V. Kresin,* University of Southern California

Bacteria produce rotary filamentous appendages, known as flagella, for propulsion through their environment in response to various chemical signals. The flagella, of nanoscale width and of microscale length, can be easily isolated from the microorganisms at low cost and in large quantities. Once isolated, these nanofilaments of uniform size distribution can be deposited onto desired surfaces in controlled quantities and can act as novel templates for nanostructures. Flagella placed on a surface ahead of ionic, size-selected metallic cluster deposition could act as scaffolds in the construction of nanocluster networks. These organized nanocluster networks could then be used to investigate the various unique quantum and nanoscale properties exhibited by finite-size systems. These include enhanced surface plasmon resonance, catalytic applications, charge tunneling junctions, and Josephson current in potential superconducting arrays.

NS-ThP8 High-contrast Infrared Polymer Photonic Crystals Fabricated by Direct Laser Writing*, **Yanzeng Li**, D.B. Fullager, S. Park,* University of North Carolina at Charlotte*; D. Childers,* USC Conec, Ltd.*; G.D. Boreman, T. Hofmann,* University of North Carolina at Charlotte

Direct laser writing has been established as a prototyping tool for the rapid fabrication of optical materials with nanometer-sized features. So far, however, highly reflective photonic crystals have been predominately obtained from 3D polymer templates manufactured by direct laser writing which were subsequently inverted using high index materials. The incorporation of high index materials enhances the reflectivity of a given 3D structure considerably, but it inevitably increases the complexity of the fabrication process. Here we demonstrate the successful fabrication of one-dimensional photonic crystals by 3D direct laser writing using only a single polymer to obtain reflectance values approaching that of a gold reference in the near-infrared spectral range. The necessary periodic variation of refractive index is achieved by utilizing partially filled layers wherein integrated sub-wavelength-sized pillars are utilized as a scaffold while simultaneously providing index contrast to that of solid polymer layers. Bruggemann effective medium theory and simulated reflectivity profiles were then used to optimize the photonic crystals' design to operate at a desired wavelength of 1.55 µm. After fabrication, the structures of the photonic crystals were compared to the nominal geometry via inspection of SEM micrographs and showed true-to-form fabrication results. A good agreement between the model-calculated and measured FTIR reflection and transmission data is observed demonstrating the ease of predictive design with this method.

NS-ThP9 Controlled Water-repellent Behavior by Modulating the Density of Nanoscale Si Nanopillar Structure Fabricated with Bio-template and Neutral Beam Etching Technique*, **Daisuke Ohori**, S. Samukawa,* Tohoku University, Japan

Si NP structures have a great potential for thermoelectric and cooling device applications. However, current fabrication techniques are too complicated. Furthermore, it is difficult to modulate the properties of the NP by those methods. In this work, we proposed an excellent method to fabricate the NP structure. The water-repellent characteristic of the fabricated Si nanopillar (NP) structure was investigated, and we try clearing the contact angle of density dependence for Si-NPs structure.

12 nm in diameter Si-NPs structure with various density ranging from 1.6 x10^{11}/cm^2 (low-density) to 7.1 x10^{11} /cm^2 (high-density) were fabricated. These samples were fabricated with a unique technique of a bio-template mask and a neutral beam etching. The bio-template mask is a protein shell with an iron oxide core, called ferritin. The density of the Si-NPs can be easily adjusted by modulating the distance between ferritins. The ferritin arrangement was carefully adjusted by controlling the length of the decorated poly(ethylene - glycol) (PEG); a spin-coating was carried out for

this arrangement process . Thereafter, an etching process was done by a neutral beam etching (NBE) technique . The NBE process could realize the damage - less etching on the surface/interface utilizing a bottom electrode that neutralize s ion in pulsed-plasma. The NBE process could realize the damage-less etching on the surface/interface utilizing a bottom electrode that neutralizes ion in pulsed-plasma. NBE can also minimize a UV irradiation to the sample which is beneficial to reduce the occuring lattice defects.

We measured the contact angle for all samples under the conditions that were the as-etch and removed SiO_2 layer. For the as-etched condition, the contact angle of the low-density and high-density samples were 4.6 and 9.1 deg, respectively. Meanwhile, the contact angle of Si wafer with a SiO_2 layer was 48.1 deg. After the removal of the SiO_2 layer, the contact angle of the low-density, high-density samples, and Si wafer became 112, 104, 89.8 deg, respectively. T his indicates that the removal of the SiO_2 layer also helps to improve the contact angle, especially the Si-NPs samples.

NS-ThP12 The TESLA JT SPM*, **Markus Maier**, D. Stahl, A. Piriou, M. Fenner, J. Koeble, K. Winkler, T. Roth,* Scienta Omicron GmbH, Germany

The TESLA JT SPM provides access to more than 5 days SPM measurement time at temperatures down to 1K (^{4}He operation) with magnetic fields larger than B > 3T. Careful thermal design of the bath cryostat and JT cooling stage as well as the integrated UHV magnet lead to exceptionally low LHe consumption of only 11 liters LHe for 120 hours, specifically also during magnet operation and field variation. The external JT Helium supply allows for ^{3}He operation and significantly lower temperatures in the range of 500mK.

The microscope head is a proven, highly stable design developed specifically for high magnetic field environments. It offers the full range of SPM measurements modes, including Scienta Omicron’s leading QPlus AFM technology.

Safe and independent tip/sample exchange under optical control is one of several key ease-of-use features delivering dependable high performance SPM and successful scientific work.

In contrast to a conventional wet magnet concept, the dry split-pair magnet provides for optical access enabling various optical experiments and even in-situ evaporation into the SPM at low temperatures.

We will discuss the technical concept and will show performance evaluation measurements at T=1K that prove stability below 1pm as well as energy resolution on superconductors.

Specifically, continuous STM and QPlus AFM imaging at varying temperatures during magnetic field ramping without increasing the LHe consumption differentiate the concept from traditional 4He and 3He systems and open up new experimental possibilities.

NS-ThP14 Novel *In-situ* Diagnostic tools to Analyze Chemical Composition and Energy Spectrum of Vapor in Thin Film Deposition Process*, **Mikhail Strikovski**, S.H. Kolagani,* Neocera LLC

The device potential of multicomponent films in various electronic, magnetic and optical applications critically depends on (i) the chemical composition and (ii) the kinetic energy of the atomic species arriving at the film growth surface. We present two novel methods and instrumentation that allow analysis and control of both composition and energy spectrum of the deposition species. Pulsed Laser Deposition (PLD), a well-known deposition method for multi component materials has been chosen to demonstrate these in-situ diagnostics, providing researchers and engineers an immediate feedback in real-time.

The first tool, called Low Angle X-ray Spectrometer (LAXS), executes quantitative analysis of multiple X-ray spectra emitted by the film-substrate system under the impact of a high-energy electron beam. As the film thickness increases, LAXS follows the evolution of the x-ray spectrum dynamically, and applies special analytical algorithm to find film composition. To validate LAXS, we have chosen multi-elemental compound Y-Ba-Cu-O and demonstrated the efficiency of the technique in identifying the deposition conditions that result in the stoichiometric YBa_2Cu_3 cation composition needed for optimum superconducting properties. In another example using Zn-Ti-Cr continuous compositional spreads, LAXS provides a 2D- map of the resulting compositions that the user can correlate with the distribution of physical properties of interest.

The second tool is the Ion Energy Spectrometer (IES), a differential retarding field energy analyzer, which probes kinetic energy distribution of ions at the growth substrate. Depending on a number of system variables, actual energetics of ions arriving at the growth surface is a critical process parameter that needs careful optimizations. As an example, we analyze the energy spectrum of CeO_2 as a function of oxygen partial pressure in a typical PLD case. Ions of energy as high as >100 eV are present, while majority of the ions are distributed in the 5 - 40 eV range. By varying oxygen background pressure, the IES spectrum is fine-tuned to have a spectral maximum at ≤10 eV- desirable for non-thermally activated, yet soft film growth. The IES also provides several operational modes, including quick acquisition of Time-Of-Flight spectrum.

NS-ThP16 High Fidelity and Sustainable Anti-reflective Moth-eye Nanostructures and Large Area Sub-wavelength Applications*, **Shuhao Si**,* Technische Universität Ilmenau, Germany*; M. Hoffmann,* Ruhr-Universität Bochum, Germany

The eyes of moths own a feature of unique significance that they reflect little or no light. The dome-like patterns in a depth of approximately 200 nm with pitches of about 200 nm function as a surface with graded refractive index to reduce the reflections.

In recent years, the booming of large screen TVs and smart phones brings increasing attentions for the AR moth-eye structures in sub-wavelength for panels. The AR moth-eye structures applied on smart phone glass displays require finer high resolution and well-oriented patterns, as well as much higher ability to sustain finger frictions and environmental contamination. However, the ideal moth-eye like structure is acknowledged to be parabolically curved domes, which has been rarely systematically demonstrated, and the reported methods suffer from the long-term sustainability. Formed by coating, those reported nanoparticles spheres can be easily peeled off from the surface inevitably by scratching or sticking in either hard or soft pressing from the first steps. The sustainability and reproducibility, thus the reduction of total cost of ownership, are strongly hindered as a consequence. Therefore, such critical issues have not been properly tackled.

An attempt has been made in this work to focus on the sustainability and reproducibility of the moth-eye structures fabricated in profile of parabolically curved domes. A master defining the resolution of the sub-wavelength structures is prepared, commonly by means of EBL. The transfer of large area moth-eye nanostructures is conducted by soft UV-NIL. The next critical step is to etch the substrate for sloping sidewalls, i.e. in an isosceles trapezoid from a cross-sectional view. After that, the silicon substrate is thermally oxidized, in which way the domes can be achieved taking advantage of the variation of oxidation rate at the structure corner, sidewall and bottom. By this step, a template featuring highly ordered moth-eye nanostructures in profile of parabolically curved dome of sub-wavelength resolution is well defined. The moth-eye patterns will be transferred onto the target glass substrate though soft UV-NIL and subsequent processing. The dome structures are made eventually in the substrate via covalent bonding, rather than physical adhesion in case of nanoparticle spheres. Loss of nanoparticles due to pressing, sticking, scratching and so on is hardly an issue.

The moth-eye nanostructures patterned in glass are expected to show improved reflectivity of the incident sunlight in sub-wavelength application of portable electrical devices such as smart phone glass displays. Soft UV-NIL enables its potential for direct large area replications.

NS-ThP18 Indirect Transition and Opposite Circular Polarization of Interlayer Exciton in a MoSe2/WSe2 van der Waals Heterostructure*, **Hsun-Jen Chuang**[1], A.T. Hanbicki, M. Rosenberger, C.S. Hellberg, S.V. Sivaram, K.M. McCreary, I. Mazin, B.T. Jonker,* Naval Research Laboratory

Indirect transition and opposite circular polarization of Interlayer Exciton in a MoSe2/WSe2 van der Waals Heterostructure

Hsun-Jen Chuang, A.T. Hanbicki, M.R. Rosenberger, C. Stephen Hellberg, S.V. Sivaram, K.M. McCreary, I.I. Mazin, and B.T. Jonker

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An emerging class of heterostructures involves monolayer semiconductors such as many of the transition metal dichalcogenides (TMDs) which can be combined to form van der Waals heterostructures (vdWHs). One unique new heterostructure property is an interlayer exciton (ILE), a spatially indirect, electron-hole pair with the electron in one TMD layer and the hole in the other.

In this report **[1],** we use state-of-the-art preparation techniques **[2]** to create MoSe2/WSe2 heterostructures encapsulated in hBN. We observe ILE emission around 1.35 eV at room temperature and resolve this emission into two distinct peaks (ILE1 and ILE2) separated by 24 meV at

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[1] **NSTD Postdoc Finalist**

zero field at 5 K. Furthermore, we demonstrate that the two emission peaks have *opposite* circular polarizations with up to +20% for the ILE1 and -40% for ILE2 when excited by circularly polarized light. A*b initio* calculations provide an explanation of this unique and potentially useful property and indicate that it is a result of the indirect character of *both* electronic transitions. These peaks are *double indirect* excitons. *i.e.* indirect in both real and reciprocal space, split by relativistic effects.

This work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #AOARD 14IOA018-134141. This work was also supported in part by a grant of computer time from the DoD High Performance Computing Modernization Program at the U.S. Army Research Laboratory Supercomputing Resource Center.

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NS-ThP21 The Silicon Atomic Layer Etching by Two-step PEALD Consisting of Oxidation and $(NH_4)_2SiF_6$ formation*, E.-J. Song,* Korea Institute of Materials Science, Republic of Korea*; J.-H. Ahn,* Korea Maritime and Ocean University, Republic of Korea*; **Jung-Dae (J.-D.) Kwon**,* Korea Institute of Materials Science, Republic of Korea*; S.-H. Kwon,* Pusan National University, Republic of Korea

The process of precise silicon etching on the atomic scale was investigated by examining the formation of an $(NH_4)_2SiF_6$ thin film as an intermediate phase followed by the removal of this layer by sublimation. An amorphous $(NH_4)_2SiF_6$ thin film was formed on a Si substrate via a two-step plasma-enhanced atomic layer deposition (PEALD) process consisting of an oxidation step involving an O_2 plasma and a transformation step to deposit an $(NH_4)_2SiF_6$ thin film using an NH_3 / NF_3 plasma, where the deposited thin film was removed by a sublimation process. Because the thickness of the $(NH_4)_2SiF_6$ thin film could be linearly controlled by altering the number of PEALD cycles, the etching depth could be successfully controlled on the sub-nanometer scale.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room Hall B - Session SA-ThP

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic Poster Session

SA-ThP1 Relative Sensitivity Factors in Hard X-ray Photoelectron Spectroscopy up to 10 keV for Quantitative Analysis*, **Satoshi Yasuno**,* Japan Synchrotron Radiation Research Institute, Japan*; N. Ikeno,* Aichi Synchrotron Radiation Center, Japan*; H. Oji,* Nagoya University Synchrotron Radiation Research Center, Japan

Hard X-ray photoelectron spectroscopy (HAXPES) has been attracting considerable attention since it can probe the chemical and electronic states of the bulk and buried interface lying at depths of several tens of nm due to its large probing depth.[1] In the last decade, HAXPES have been applied to various research fields, such as electronic devices, organic materials, and rechargeable batteries. However, the quantitative analysis of the HAXPES measurement related to the relative sensitivity factors(RSFs), standard materials and theoretical calculations in hard X-ray region, have not previously been reported in detail. Therefore, in this study, we investigated the procedures of quantitative analysis for HAXPES and development of the RSFs data base in the hard X-ray region. Here, we focused the database of the RSFs of compounds provided by Wagner.[2] According to Wagner's RSFs principle, the absolute value of the sensitivity factor will vary with the matrix because of the variability of the mean free path λ, by contrast the relative sensitivity factor will hardly vary because the ratio λ_1/λ_2 for element 1 and 2, is only slightly with matrix dependence. Therefore, with the RSFs of compounds, the corrections related to the mean free path which largely influenced the number of photoelectron (signal intensity) are not needed for the quantitative analysis. For HAXPES, the core level peaks can be measured in a wide kinetic energy. Thus, it is suggested that the RSFs obtained by the compound is suitable for HAXPES measurement. In this study, the empirical sensitivity factors for the 1s, 2s, $2p_{3/2}$, $3d_{5/2}$ and 4f levels relative to O 1s were derived from HAXPES measurements with the photon energy of 6, 8, 10 keV. Comparing with the theoretical RSFs calculated from Hartee-Slater cross sections reported by Scofield with combined energy dependence on the spectrometer function and the inelastic mean free path, the good agreement between the empirical and the theoretical RSF values were observed with several notable exceptions, while the discrepancies were observed in several energy regions.

Acknowledgement

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SA-ThP2 In Situ Characterization of Freeze-Cast Metal Nanowire Aerogels*, **Tyler Fears**, J.A. Hammons, F. Qian, T. Braun, A.L. Troksa, M.H. Nielsen, J.B. Forien, T.F. Baumann, T.Y. Han, S.O. Kucheyev, M. Bagge-Hansen,* Lawrence Livermore National Laboratory

Metal nanowire aerogels are a new class of nanoporous materials desirable for a number of applications in energy storage, generation, and utilization. These materials are made by freezing suspensions of high-aspect-ratio (a ≈ 1000) metal nanowires and gently removing the solidified matrix, e.g., via freeze-drying, to prevent collapse of the porous nanowire network. As such, the porosity in the final aerogel is intrinsically linked to solvent phase separation and crystallization during freezing which is highly sensitive to the conditions under which it takes place, e.g., temperature, solvent composition, and sample geometry.

Herein will be discussed recent developments at Lawrence Livermore National Laboratory to produce high-quality ultra-low-density (1-30 mg/cm^3) metal aerogels via a facile freeze-casting approach. Due to the hierarchical structure of the aerogels (1-100 µm micropores in a nanoporous matrix of 3-30 nm diameter nanowires) it was necessary to use a wide variety of complementary in situ/ex situ analysis techniques to ascertain the structure and origin of these hierarchical features. This presentation will discuss the unique properties of these aerogels and the advanced analysis techniques used in their characterization, e.g., USAXS/SAXS/WAXS, X-ray tomography, XPS, optical microscopy, and electron microscopy. This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

SA-ThP3 In situ Probing of the Potential Distribution in a Thin Film All-solid-state Li-ion Battery*, **Evgheni Strelcov**,* National Institute of Standards and Technology (NIST)/University of Maryland*; E.J. Fuller,* Sandia National Laboratories*; W. McGehee, N.B. Zhitenev, J. McClelland,* National Institute of Standards and Technology (NIST)*; A. Talin,* Sandia National Laboratories

The next generation of portable electronic devices, electric vehicles, power grids, and robots require safer, smaller, lighter, cheaper, and more stable batteries. Of special importance are all-solid-state power sources that do not use conventional, flammable electrolytes and are intrinsically safer. Rational design of such batteries is challenging without in-depth understanding of the chemical and physical processes in electrochemical cells at the microscopic, nanoscopic, and eventually, atomic levels. Particularly important structural elements of solid-state Li-ion batteries (SSLIBs) that control the overall device performance are the interfaces that form between the electrodes and the cathode/anode materials and solid electrolyte. Despite decades of studies with classical electrochemical techniques, spectroscopic and microscopic tools, the interfacial characteristics of batteries, including the origins of high impedance often observed at solid state interfaces, are still poorly understood. Here, we employ in situ Kelvin Probe Force Microscopy (KPFM) to probe the potential distribution in a SSLIB as a function of its charge state. The battery was fabricated by sequentially depositing thin layers of Pt (110-130 nm), $LiCoO_2$ (280-420 nm), LIPON (1100-1200 nm), Si (50-240 nm) Cu or Pt (150-200 nm) onto a Si/SiO_2 wafer (oxide thickness 100 nm). The fabricated battery was cleaved in an Ar atmosphere to expose the stacked layers, mounted on a holder, wired, and safely transferred without exposing to air into a dual-beam instrument that combines a scanning electron microscope (SEM), a Ga-ion focused ion beam (FIB) and an atomic force microscope (AFM) in one vacuum chamber (residual pressure of 10^{-4} Pa). The stacked battery was milled to expose a cross-section of the layers, and imaged using SEM and KPFM, while cycling the battery. The acquired potential maps reveal a highly non-uniform interelectrode potential distribution, with most of the potential drop occurring at the electrolyte-Si anode interface in the pristine battery. During the first charge, the potential distribution gradually changes, revealing complex polarization within the LIPON layer due to Li-ion redistribution. The acquired data shed light onto the interfacial Li-ion transport in SSLIBs and its reversibility.

ES acknowledges support under the Cooperative Research Agreement between the University of Maryland and the National Institute of Standards and Technology Center for Nanoscale Science and Technology, Award 70NANB14H209, through the University of Maryland.

SA-ThP4 A New Route for the Determination of Protein Structure in Physiological Environment through Coherent Diffraction Imaging.*, **Danny Fainozzi,*** university of Trieste / Elettra Synchrotron, Italy

Revealing the structure of complex biological macromolecules, such as proteins, is an essential step for understanding the chemical mechanisms that determine the diversity of their functions. Synchrotron based x-ray crystallography and cryo-electron microscopy have made major contributions in determining thousands of protein structures even from micro-sized crystals. They suffer from some limitations that have not been overcome, such as radiation damage, the natural inability to crystallize of a number of proteins and experimental conditions for structure determination that are incompatible with the physiological environment. Today the ultrashort and ultra-bright pulses of X-ray free-electron lasers (XFELs) have made attainable the dream to determine protein structure before radiation damage starts to destroy the samples. However, the signal-to-noise ratio remains a great challenge to obtain usable diffraction patterns from a single protein molecule. We describe here a new methodology that should overcome the signal and protein crystallization limits. Using a multidisciplinary approach, we propose to create a two dimensional protein array with defined orientation attached on a self-assembled-monolayer . We develop a literature-based, flexible toolbox capable of assembling different proteins on a functionalized surface while keeping them under physiological conditions during the experiment, using a water-confining graphene cover.

SA-ThP5 The League of European Accelerator-Based Photon Sources: New strategic partnerships in Europe and beyond*, **Maya Kiskinova,*** Elettra-Sincrotrone Trieste, Italy

The grand challenges of our century to evolve from extensive wasteful development to sustainable economies is full understanding of the mechanisms which control the behavior of complex natural and man-made systems. This can be attained only through development of an integrated multidisciplinary approach. Many of the breakthroughs in investigations of a broad range of complex functional material systems have been made using the state-of-the art experimental techniques undergoing continuous developments at the synchrotron and free electron laser large scale facilities.

Recognizing the leading roles of these large scale research centers in paving the road to discoveries and further technological advancements, the recently established new research consortium in Europe called *"The League of European Accelerator-Based Photon Sources (LEAPS)"* is aiming at reaching a new level of cooperation, coordination and integration to better cope with cross-cutting scientific and technological challenges for knowledge-based design of advanced materials and better drugs. The poster will present an overview of the LEAPS strategy, goals and expected impacts in science and innovation.

Thin Films Division
Room Hall B - Session TF-ThP
Thin Film Poster Session

TF-ThP2 Investigation of Target State by Plasma Emission and Target Voltage Measurements for Reactive Sputtering of Ni oxide thin films with water vapor injection*, **Yuki Yokoiwa**, Y. Abe, M. Kawamura, K.H. Kim, T. Kiba,* Kitami Institute of Technology, Japan

Reactive sputtering is one of the most commonly used techniques for obtaining compound thin films. It is well known that target mode change is very important in reactive sputtering, because the change in the target surface state induces drastic changes in the deposition rate. In the previous study, we reported that the reactive sputtering with substrate cooling and water vapor injection was promising technique to obtain Ni oxide thin films with high-rate deposition. We speculated that the high deposition rate was realized by metallic target state. In the present study, we investigated the target state in more detail using plasma emission spectroscopy and target voltage measurements.

Ni oxide thin films were formed by a RF magnetron sputtering system. Substrate temperature was varied from room temperature (RT) to -80 °C. Ni metal target was sputtered in Ar and H_2O sputtering gas atmosphere, and the flow ratio ($H_2O/(H_2O+Ar)=RH_2O$) was varied from 0 to 100%. H_2O was injected onto the target surface. Target voltage and plasma emission spectrum were measured to investigate the target surface state during sputter deposition. Film thickness was measured using a stylus profiler. The deposition rate was calculated from the film thickness and sputtering time. The optical and electrical properties of the films were studied by UV-Vis spectroscopy and four-point prove method.

At RT, deposition rate decreased from 15-20 nm/min to 4 nm/min above RH_2O=20%. On the contrary, at -80 °C, deposition rate increased monotonously with increasing RH_2O, and a maximum deposition rate of 35 nm/min was obtained at RH_2O=50%, which was approximately 8 times larger than that at RT. Corresponding to the change of the deposition rate, target voltage decreased abruptly from 330 V to 190 V above RH_2O=20% at RT when RH_2O was increased gradually. In contrast, target voltage maintained a high value of 290-330 V at -80 °C. Plasma emission spectra indicated that emission peaks due to Ni atoms disappeared at RT above RH_2O=20%, however, the peaks were clearly observed regardless of the change of RH_2O at -80 °C. These results indicate that the Ni target changed from metallic mode to oxide mode above RH_2O=20% at RT, however, metallic target mode was maintained at -80 °C.

The optical and electrical properties of the films were studied. The films deposited at substrate temperatures of RT and -80 °C below RH_2O=10% have metallic character. And transparent and insulating Ni oxide films were obtained above RH_2O=20% at both the substrate temperatures.

In summary, reactive sputtering of Ni oxide thin films in metallic target mode was realized using substrate cooling and water vapor injection.

TF-ThP3 Rectification and Non-linearity in Ferroelectric Tunnel Junction based on $BiFeO_3$ Ultra-thin Film*, **Taekjib Choi,*** Sejong University, Republic of Korea

Intriguing polarization-mediated charge transport phenomena has driven extensive research on ferroelectric resistive memories, such as ferroelectric tunnel junction, switchable diode, and ferroelectric memristor. Recently, ferroelectric tunnel junction exhibited higher on/off ratio and lower power consumption. However, to realize high density memory devices that are compatible with cross-point stack structures, it requires high rectification and high non-linearity to prevent unwanted leakage current paths through neighboring cells (a well-known sneak path problem) in cross-point structures. In this study, we fabricated the ferroelectric tunnel junction memory device for application to highly integrated vertical memory devices. The charge conduction behavior with switching of ferroelectric polarization in $BiFeO_3$ ultra-thin films based tunnel junctions were investigated. In addition, by introducing space charge layer in ferroelectric tunnel junctions, we demonstrated enhanced rectification and non-linearity in current-voltage characteristics for Pt/$BiFeO_3$/Nb-$SrTiO_3$ tunnel junctions. It was found that on /off ratio reached to maximum 10^4. Therefore, our ferroelectric tunnel junctions showing both high resistance ratio and nonlinearity factor offers a simple and promising building block of high density non-volatile memory. This research was supported by the MOTIE (Ministry of Trade, Industry & Energy (#10080643) and KSRC (Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.

TF-ThP7 Optical and Electrochemical Properties of Rhodium Oxide Thin Films prepared by Reactive Sputtering in O_2 or H_2O Atmosphere*, **ChanYang Jeong**, Y. Abe, M. Kawamura, K.H. Kim, T. Kiba,* Kitami Institute of Technology, Japan

Platinum group metal oxides, such as iridium (Ir) oxide, ruthenium (Ru) oxide, rhodium (Rh) oxide have been studied for electrochemical applications, because of their high chemical stability and electrical conductivity. However, reports on Rh oxide thin film were very scarce compared to Ir oxide and Ru oxide thin films. In this study, we investigated density, structure and optical properties of Rh oxide thin films and their effects on electrochemical properties.

Rh oxide thin films with a thickness of 100 nm were prepared by sputtering a Rh metal target in O_2 or H_2O atmosphere on glass, Si, and ITO-coated glass substrates. The substrate temperature was varied from -20 to 130 °C using a Peltier device. The density of the films was measured by X-ray reflectivity (XRR). Crystal structure and chemical bonding state of the films were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR), respectively. Optical properties were measured by UV-Vis spectroscopy. Electrochemical properties of the Rh oxide thin films were measured in 1M KOH aqueous electrolyte.

From the XRR measurements, the density of the films deposited in H_2O atmosphere was found to be lower than that deposited in O_2. The density of the films decreased with decreasing substrate temperature and the lowest density of 4.2 g/cm^3 was observed for the film deposited at -20 °C in H_2O atmosphere. XRD pattern showed that all the films except for the film deposited at 130 °C in O_2 atmosphere were amorphous. From the FT-IR spectra, absorption peaks of Rh-O and O-H bonds were observed on all the films. Higher transmittance was obtained for the films deposited in H_2O atmosphere compared to that the of films deposited in O_2. It was also found that the transmittance of the films increased with decreasing the substrate temperature, which suggests that the films were partially hydrated. As a result of the cyclic voltammetry measurements, the larger transferred charge density (ΔQ) was obtained for the films deposited in the H_2O atmosphere compared to that of the films deposited in O_2. And the largest ΔQ of 13 mC/cm^2 was obtained for the film deposited at -20 °C in H_2O atmosphere.

In summary, it was found that the Rh oxide thin film deposited at -20 °C in H_2O atmosphere had the lowest density and showed the highest electrochemical activity.

TF-ThP8 Interfacial Self-assembled Monolayers as Copper Diffusion Barrier for IGZO Semiconductor Thin Film Transistor*, **Sung-Eun Lee**, K.-H. Lim, J. Park, J.-E. Huh, J. Lee, E.G. Lee, C.I. Im, Y.S. Kim,* Seoul National University, Republic of Korea

Copper (Cu) is used in many electrode industrials because of its relatively low resistance and cost competitiveness compared to other metals. Particularly, since semiconductor and display devices require low-resistance electrodes with a high integration, interest in Cu has been more increasing. On the other hand, due to the inherent diffusion tendency, it is known that the Cu ion can easily migrate into Si or oxide based semiconductor and generate reactant with a high resistance at the interface. Thus, deterioration such as hump or abnormal current phenomenon may be occurred. To alleviate the disadvantages, diffusion barriers such as Mo, Ti and various metal alloys with hundreds of nanometer-thick or more have been used so far with micrometer size Cu electrode. However, because of the high integration of devices, the Cu electrode might soon be less than a few hundred nanometers, similar to the physical dimension of metal barrier mentioned above. Ultimately, it would be urgent to develop down sized diffusion barriers of less than ten nanometers in order to take advantage of Cu properly.

Self-assembled monolayer (SAM) is a thin film with a few nanometers to control surface of the material. Recently, many researchers study on SAM as a barrier to prevent migration of Cu ions and electrons onto dielectrics such as SiO_2. In this study, several functional groups of CH_3, SH, CF_3, and NH_2 SAM diffusion barriers located between IGZO and Cu were investigated in order to not only prevent migration of Cu ions, but also transfer electrons. As a result, there was no hump or abnormal current phenomenon occurring, therefore it was confirmed that the SAMs can prevent Cu ions migration and transfer electrons. The results of the TFT characteristic were measured similarly at whole functional groups, but the SAMs containing carbon in the functional groups such as CH_3 and CF_3 showed definitely superior performance in the hysteresis measurement.

We also confirmed that a few properties can be controlled by the body group chain length of the SAM verified by the hysteresis, transmission line method (TLM) and SIMS analysis. In other words, the TFT characteristics can be improved or deteriorated with body group chain length of SAM, and we found that it is very important to determine the proper length. This result is expected to have an important impact on the application of Cu electrode in semiconductor devices in the future.

TF-ThP9 Atmospheric-pressure Plasma Treatment Effect of Solution-processed Aluminum Oxide Gate Insulator for Oxide Semiconductor Thin-film Transistors*, **Jintaek Park**, K.-H. Lim, S.-E. Lee, J.-E. Huh, J. Lee, E.G. Lee, C.I. Im, Y.S. Kim,* Seoul National University, Republic of Korea

Solution-processed thin-film transistors (TFTs) have received great attention as a next generation display manufacturing method, because they do not require cumbersome equipment compared to the vacuum process and can be applied to the roll-to-roll process. Therefore, oxide semiconductors such as InO_x using aqueous route method have been studied in a simple and inexpensive process. However, most of the research is confined to the semiconductor thin film, and the research on the gate insulating film which is indispensable for the constitution of the TFT device is insufficient.

In general, high-k materials such as AlO_x, HfO_x, and TaO_x have been used as dielectric layers because they can provide large gate capacitance without significantly increasing gate leakage current. Among all high-k dielectric materials, AlO_x is widely used because of its low deposition temperature, low cost, and good compatibility with oxide semiconductors.

In this study, AlO_x using aqueous route method was deposited by a solution process and its characteristics were evaluated. Characteristic changes through atmospheric-pressure plasma treatment were observed by measurement of capacitance-frequency and breakdown voltage. It was observed that the frequency dependence of AlO_x capacitance was reduced by atmospheric-pressure plasma treatment. In general, the frequency dependence of the AlO_x capacitance is because of the ions in the layer limit the polarization response time. Thus, the changes of binding relationship according to plasma treatment time were analyzed by X-ray photoelectron spectroscopy (XPS). In addition, TFTs were fabricated by depositing a solution-processed InO_x with a semiconductor film, and the characteristics were evaluated. It was observed that field-effect mobility increased from 6.7 to 15.1 compared to the untreated samples. The surface roughness of the AlO_x films was investigated by atomic force microscopy (AFM). Semiconductor and gate dielectric fabrication, and plasma processing were performed in a non-vacuum environment and the process temperature was below 250 ℃

TF-ThP10 Microstructural and Electrical Properties of Ni Stanogermanides formed on $Ge_{0.92}Sn_{0.08}$ epi-layer Grown on Si(100) Substrate*, **HanSoo Jang**,* Semiconductor Physics Reasearch Center(SPRC), Chonbuk National Universityh, Republic of Korea

We present a comprehensive study on the microstructural and electrical properties of Ni stanogermanides formed on $Ge_{0.92}Sn_{0.08}$ epi-layer grown on Si(100) substrate. For the formation of Ni-stanogermanides, 30 nm-thick Ni film was deposited on $Ge_{0.92}Sn_{0.08}$ film, followed by rapid thermal annealing (RTA) process at the temperatures in the range of 300 – 600 °C for 30 s under N_2 ambient. Ni-rich stanogermanide ($Ni_3(Ge_{1-x}Sn_x)$) phase with cubic structure was formed after RTA at 300 °C, above which Ni-mono stanogermanide ($Ni(Ge_{1-x}Sn_x)$) was the only phase formed as a result of solid-state reaction between Ni and $Ge_{0.92}Sn_{0.08}$. The RTA process at 400 °C led to the formation of $Ni(Ge_{1-x}Sn_x)$ film having relatively uniform surface and interface morphologies, allowing the minimum value of sheet resistance. The samples annealed above 500 °C underwent the severe structural degradation of $Ni(Ge_{1-x}Sn_x)$ without maintaining film continuity known as agglomeration, resulting in a rapid increase in the sheet resistance. Regardless of RTA temperature, secondary ion mass spectroscopy (SIMS) results combined with energy dispersive X-ray spectroscopy (EDX) line profiling showed the segregation of Sn atoms near surface and interface region, indicating that the amount of Sn atoms were out-diffused during Ni-stanogermanides process. In particular, laterally confined Se atoms which were distributed along interface between $Ni(Ge_{1-x}Sn_x)$ island and $Ge_{0.92}Sn_{0.08}$ film was observed in the sample annealed at 600 °C.

TF-ThP11 Radiation Effects on Al_2O_3 Thin Films*, H.P. Zhu, X. Chen, **Zhong-Shan Zheng**, D.L. Li, J.T. Gao, B. Li, J.J. Luo,* Institute of Microelectronics of Chinese Academy of Sciences, China

The radiation response of Al_2O_3 thin films is investigated using Co-60 gamma rays and energetic Si ions. The Al_2O_3 thin film was prepared on Si substrates with ALD processes, and Al/ Al_2O_3/ Si structures were used to observe radiation effects on the Al_2O_3 dielectric film by the capacitance–voltage (C-V) technology. The results show that there are a lot of hole traps in the ALD Al_2O_3 film, which can be mainly attributed to oxygen vacancy (V_O) defects by calculation analyses based on the first-principles, and total dose effects are also apparent for the Al_2O_3 film irradiated using energetic Si ions at higher fluence levels. In particular, the combined impact of gamma rays and energetic Si ions on the Al_2O_3 film is examined at the same time, and the results suggest that electron traps can be introduced in the Al_2O_3 film due to Si ion irradiations.

TF-ThP12 Comparative Study of Erosion on Various Polymers and Composites both Coated Using a DC Magnetron Sputtering Process and Uncoated*, S. Hill, **Dorina Mihut**, A. Afshar, K.J. Culp, Z. Grantham,* Mercer University School of Engineering

Solid particle impact erosion is a progressive loss of the materials' mass that results from repeated impact of the erodent on the material surface. Materials selection for equipment working in this type of aggressive environmental conditions is a great challenge. These materials must possess some resistance to erosion and have high strength, hardness, toughness, and good corrosion resistance. It would be advantageous to select a lightweight material with good strength and corrosion resistance; however these materials are have limited resistance to impact erosion. Some examples of these types of materials are polymers and composites. However, in some cases, it is necessary to coat the polymers with a metallic coating to enhance certain properties of the materials. This study uses an impact erosion tester to study the effect of accelerated erosion on different polymers, composites, and metallic coated polymers and composites. A two phase mixture is circulated in a custom test fixture and allowed to impact test coupons at specified angles. The study uses three sand concentrations, a fixed liquid flow rate, and a constant impact angle during testing to determine the effect of the material's properties on the amount of erosion. The metallic coatings on the samples are aluminum, copper, and titanium and were deposited using DC magnetron sputtering equipment and the structures of the coatings was characterized using X-Ray diffraction.

TF-ThP13 Plasma-enhanced Atomic Layer Deposition of Molybdenum Compounds Thin Films Using Mo(CO)$_6$ with Various Plasma Gases*, Jeong-Hun Choi*, *S.W. Lee, C.M. Hyun, J.-H. Ahn,* Korea Maritime and Ocean University, Republic of Korea

In recent years, transition metal oxides and dichalcogenides have received much attention due to its attractive properties for a wide range of applications. Among these materials molybdenum compounds were studied most initiatively and achieved considerable progress. Meanwhile, metallic molybdenum is also widely used as conducting materials in many electronic applications. In this study, therefore, optical, structural and electronic properties of metallic molybdenum and its compounds thin films have been investigated. Plasma-enhanced atomic layer deposition (PEALD) was employed to form the uniform Mo, MoO_3, MoS_2 thin films. Especially, When $Mo(CO)_6$ was used as the precursor, different kinds of plasma gases such as O_2, H_2, H_2S and their mixtures for reactant resulted in selective growth of Mo, MoO_3, MoS_2, respectively. Basically, the ALD characteristics with each reactant were studied. The ellipsometry, raman spectroscopy, photo luminescence, X-ray photoelectron spectroscopy, scanning electron microscopy were used to examine film characteristics according to the different precursor combinations and growth conditions. Furthermore, the potential of metallic Mo as well as Mo compounds for device component was investigated.

TF-ThP14 Development of Metal Linear Evaporator for OLED Panel Mass Production of Gen.6 half and Gen. 8 lines*, **Jung Hyung Kim**,* Korea Research Institute of Standards and Science (KRISS), Republic of Korea*; M.S. Kang, K.S. Shin, D.M. Lim,* Fineva Co., Republic of Korea

In the OLED processes, the metal layer such as Ag, Mg, or Al need to be deposited on the substrate for forming cathode. Usually metal layer is deposited by using a sputtering method in LCD panel processes. In the OLED processes, we cannot use sputtering method because of charge damage on the organic layer from the plasma. We can use only the evaporation method for the deposition of metal layer. A point evaporator has been used for metal layer deposition in the OLED process. In Gen. 6 half mass production line, the substrate hung from the ceiling is rotated to acquire good uniformity of the deposition film. In Gen. 8 mass production line, point evaporators are arrayed and the substrate is scanned on the ceiling. These method of rotation and arrays are difficult to get good uniformity. Since the distance between evaporator and substrate is very long about 1000 mm, metal usage is very low about 10 %. Therefore, the demands of metal linear evaporator has been very high in the field of mass production lines. We developed a metal linear evaporator for OLED panel mass production of Gen 6 half and Gen. 8 lines. The heating method is an inductive heating with a few tens kHz of frequency and the crucible of one body is graphite. The distance between the evaporator and the substrate is less than 500 mm. The direction of evaporation is bottom-up. The uniformity of Ag film deposited with the deposition rate of 5 A/s is less than 5 % in the length of 900 mm. Our technology can be extended to a vertical type or top-down evaporator.

TF-ThP16 Fabrication of Mo/B_4C Periodic Films on the High Reflective Mirror for Applications in Beyond Extreme Ultraviolet Lithography*, Chao-Te Lee*, *W.-C. Chen, H.-P. Chen, M.-K. Wang,* Instrument Technology Research Center, Taiwan, Republic of China

The extreme ultraviolet lithography (EUVL) is based on all-reflective optics operating at wavelength of 13.5 nm, was been proposed the new lithographic systems for the semiconductor industry. Beyond extreme ultraviolet lithography (BEUL), the center wavelength of 6.7 nm, is also being considered as the next generation of EUVL. In this study, the absorber layer (Mo) and space layer (B_4C) materials with various complex refractive index were been used to design the periodic films application in BEUVL at 6.7 nm wavelength by RF magnetron sputtering system. The effects of working pressure, RF power, and substrate bias on the microstructure, roughness and optical properties of films were investigated by field emission scanning electron microscopy, X-ray diffraction, atomic force microscopy, high resolution transmission electron microscope, and EUV spectrometer. The possibility of absorber layer/space layer periodic films application for BEUVL optical device with high reflectance was also investigated.

TF-ThP17 Effects of the Electric Field Application for the Photocatalytic Property of TiO_2/Ni Thin Films*, **Taishi Segawa**, I. Takano,* Kogakuin University, Japan

In recent years, titanium oxide (TiO_2) has been attracting attention by its various properties and has been studied in a wide field such as application to solar cells or medical instruments. One of the reasons why TiO_2 is the superior material as a photocatalyst is that the photo-excited state is very stable and does not cause autolysis. Therefore TiO_2 irradiated with ultraviolet rays can make the electrolysis of water stably proceed. On the other hand, the inferior point of TiO_2 is that the absorption wavelength is limited to the ultraviolet region under 380 nm. Therefore, many researchers have studied to improve the efficiency of the light reaction of TiO_2. The distinctive point of our study is the energy supply of electricity with the light irradiation. In this report, the optimum conditions of each film thickness and applied voltage were examined.

In this study, the glass substrates of 15 × 9 mm cleaned by an ultrasonic cleaner with acetone for 5 minutes were used. The TiO_2/Ni thin films were prepared by the multi-process coating apparatus with magnetron sputtering sources. The TiO_2 thin film preparation was carried out by sputtering a Ti target introducing an Ar and an O_2 gas. An Ar gas and an O_2 gas flow rate were set to 1.5 sccm and 20 sccm, respectively. The glass substrates were heated to 200 degrees by an infrared heater. The film thicknesses of TiO_2 were changed with 0 - 200 nm and Ni were changed with 25 - 100 nm to investigate the suitable condition.

The crystal structure of each thin film was analyzed by X-ray diffraction. Optical properties were measured using a UV-Visible spectrophotometer. The photocatalytic properties were measured by a methylene-blue immersion test under irradiation of the artificial sunlamp (visible light) for 2 hours. The change of the methylene-blue transmittance was measured using a UV-Visible spectrophotometer.

In this study the change of the methylene-blue transmittance was regarded as the effect of photocatalytic characteristics. The transmittance of a voltage application showed 8 times from 4 times as compared with the case of an unapplied voltage. The transmittance of a methylene-blue solution for the TiO_2/Ni (200/100) thin film showed the highest value of 48 % by a voltage application. On the other hand, the applied voltage dependence of the TiO_2/Ni (200/100) thin film showed the highest value at 2.0 V in an applied voltage. Over 2.0 V of an applied voltage, the transmittance of a methylene-blue solution gradually decreased. It was considered that the recombination of electrons and holes was delayed by applying a voltage of an appropriate value.

TF-ThP18 Crystallization Behavior and Thermal Stability of Zr-based Metallic Glasses*, J.S. Park, D.H. Song, **JinKyu Lee**,* Kongju National University, Republic of Korea

Metallic glasses have attracted significant attention over recent year because of their unique properties such as high strength, superior magnetic properties and super-plasticity. Since the metallic glasses crystallize by a nucleation and growth process, crystallization process offers a unique opportunity of study under controlled conditions of the growth of crystals. It also provides information of the relative thermal stability of metallic glasses. As well as, study on the crystallization behavior of metallic glasses will help to control and optimize the properties of metallic glasses. Recently, for practical applications, thin film metallic glass coating by sputter deposition seems to be an alternative way for the application of metallic glass.

In this study, we report the thermal stability and crystallization behavior of Zr-based metallic glasses. Zr-based metallic glasses were fabricated by melt spinning and RF magnetron sputtering, respectively. Structural characterization of metallic glasses was investigated by X-ray diffractrometry, scanning electron microscopy and transmission electron microscopy. Thermal stability was investigated by differential scanning calorimetry during the continuous heating and isothermal annealing modes in the supercooled liquid region. Mechanical properties were determined by nano-indentation experiments using the continuous stiffness measurement method.

TF-ThP19 The Investigation of the Chemical State of the PTFE Surface Treated by Ar Plasma*, **Koki Iesaka, I. Takano,* Kogakuin University, Japan

Polytetrafluoroethylene (PTFE) has excellent characteristics such as low friction coefficient, flame retardancy, electrical insulation, chemical resistance, etc. By utilizing these characteristics, PTFE is applied in various fields such as semiconductors, chemical plants, automobiles, etc. Furthermore, improvement of water repellency or hydrophilicity for PTFE leads to development of a new material with high-performance characteristics or a wider application.

In this study, two types of PTFE were used as samples. Those were a fluororesin adhesive tape (NITTO) referred as T-PTFE in this paper and a NAFLON sheet (NICHIAS) referred as N-PTFE. The experimental conditions were 120 - 1200 s in an irradiation time and 50 - 200 W in an RF input power of Ar plasma under an ultimate pressure of < 6.0×10^{-6} Pa. The observation of the surface morphology was carried out by a laser microscope (OLS 4500; OLYMPUS Co. Ltd.) and a field emission Auger micro probe (JAMP-9500F; JEOL Ltd.). The determination of the surface characteristics was carried out using a contact angle meter (DM-300; Kyowa Kaimen Kagaku Co. Ltd.) about a contact angle of water and X-ray photoelectron spectroscopy (ESCA-K1S; SHIMADZU Co. Ltd.) about a surface chemical state.

In the case ofN-PTFE, the surface C and O atomic concentration measured by X-ray photoelectron spectroscopy gradually increased until 120 s in an Ar plasma treatment time. Over 120 s those concentration gradually decreased and approached those of the untreated N-PTFE at 600 s. On the other hand, from the contact angle measurement of water, the surface characteristic gradually changed to hydrophilicity until 120 s as compared to the untreated N-PTFE. It was considered that the CF_2 bonds of PTFE which induced water repellency decreased by preferential sputtering of F and the free bonds of C absorbed O_2 of the air or H_2O.

The large treatment energy such as ion beams caused the formation of the needle-like morphology, while the low energy of Ar plasma changed only a chemical state regardless of a treatment time. It became clear that the treatment energy for the stable polymer like PTFE influenced the chemical state or the morphology.

TF-ThP20 The Influence of ZnO Layers for Photovoltage of $Cu_2O/ZnO/TiO_2$ Thin Films Prepared by Reactive Sputtering*, **Keisuke Ishizaka**,* Kogakuin University,Japan*; I. Takano,* Kogakuin University, Japan

As one of solution methods of the power shortage and global warming, a renewable energy such as solar cells is desired. In addition the high purity silicon that is the main raw material for solar cells is insufficient worldwide, and so new solar cells without silicon that are able to be replaced to silicon-based solar cells have been required. Practical application of oxide-based thin film solar cells is expected in reduction of the energy cost or the environmental load.

Generally a typical oxide-based thin film solar cell is known as a wet dye-sensitized solar cell composed of an electrolyte, an electrode of a titanium oxide and a sensitizing dye. Recently a solid-state dye-sensitized solar cell which uses metal oxides instead of an electrolyte has been studied. In our previous study on Cu_2O/TiO_2 solid-state dye-sensitized solar cells, the main problem was Cu diffusion from a Cu_2O layer to a TiO_2 layer. Because the diffusion of Cu to a titanium oxide layer induces the collapse of p-n junction, various materials as an intermediate layer between Cu_2O and TiO_2 have been attempted.

The ZnO layer used in this study has characteristics of a transparent oxide semiconductor, a low electrical resistivity or an n-type semiconductor. Especially the ZnO layer show a lower value about an electrical resistivity than the NiO layer or the TaON layer which had been used in the previous study.

$Cu_2O/ZnO/TiO_2$ solar cells were fabricated by reactive magnetron sputtering. As substrates, the EAGLE XG glass and the ITO-film coated glass were ultrasonically cleaned by acetone. The oxide layers were deposited on those substrates by using pure metals as a sputtering target material in an oxygen gas atmosphere. The flow rate of an argon gas for sputtering was kept at 15 sccm of Cu_2O, and at 20 sccm of TiO_2 and ZnO. The flow rate of an oxygen gas for sputtering was kept at 1.5 sccm of TiO_2, and at 10 sccm of Cu_2O and ZnO A thickness of a TiO_2 and a Cu_2O layer was kept at 200 nm, while a thickness of the ZnO layer was changed from 2 nm to 50 nm. $Cu_2O/ZnO/TiO_2$ solar cells were successfully fabricated by reactive magnetron sputtering. The investigation of $Cu_2O/ZnO/TiO_2$ solar cells were carried out by an x-ray diffraction, a spectrophotometer and a field emission Auger microprobe.

TF-ThP21 The Formation of Amorphous Carbon Thin Films by Ion Beam Mixing*, **Kenji Iwasaki**, I. Takano,* Kogakuin University, Japan

Recently, single-layer graphene sheets, diamond films or carbon nitride films have attracted attention as high-functional materials containing carbon. Among them, Diamond-Like Carbon (DLC) is an amorphous carbon film showing superior characteristics which are close to diamond. Since those characteristics are high hardness, low friction coefficient, etc., amorphous carbon is used in a wide range of mechanical fields such as machine parts or engine parts. On the other hand, as new characteristics of amorphous carbon, the gas barrier or the biocompatibility is studied and amorphous carbon is also applied to food containers or medical instruments.

Amorphous carbon films are fabricated by various methods such as physical vapor deposition or chemical vapor deposition. Because almost amorphous carbons have the high internal stress, the adhesion between the formed carbon film and the substrate became often a important problem. In our studies, amorphous carbon films have been formed by using the ion beam irradiation in a hydrocarbon gas atmosphere to improve the adhesion between the carbon film and the substrate. Generally it is known that the mixing layer in interface of a substrate is formed by high energy ions. In the experiment of the ion beam mixing method, the multi-process coating apparatus with a mass analyzer of 45 degrees in a beam line from the Freeman type ion source was used. C_2H_2 used as an atmosphere gas has a higher deposition rate than other hydrogen gases such as ethylene (C_2H_4) or methane (CH_4).

In the experiment, an N^+ or an N_2^+ ion beam was irradiated in a C_2H_2 atmosphere to various substrates (Stainless steel, Al, Cu, Si) at conditions of 20 kV in an ion energy and of 2 - 10 mA/cm^2 in an ion current density. Obvious depth profiles of N element was obtained by a field emission Auger micro probe, while the slight deposition of amorphous carbon on the surface of each substrate was observed regardless of a value of an implanted N element.

TF-ThP22 Enhancing Ultra-violet Optical Properties of Aluminum Mirrors with a Single Step Approach to Oxide Removal and Fluorine Passivation*, **David Boris**,* U.S. Naval Research Laboratory*; A.C. Kozen,* ASEE Postdoctoral Fellow*; J. del Hoyo, M.A. Quijada,* NASA Goddard Space Flight Center*; S.G. Walton,* U.S. Naval Research Laboratory

Astronomical measurements in the Far Ultra-violet (FUV, 90-200nm) have typically relied on aluminum thin films due to aluminum's high reflectivity over this wavelength range. Unfortunately, the native aluminum oxide layer formed in atmosphere is strongly absorbing in this wavelength range, requiring that the aluminum films be passivated with a dielectric that inhibits oxidation. Due to the fast oxidation of aluminum, a simultaneous etch and deposition process is required to both eliminate the native aluminum oxide after growth and replace it with a different passivation coating layer. Optical measurements in the FUV range are some of the most challenging due to limited selection of low reflectivity coatings available for use on aluminum thin films. Typically magnesium fluoride (MgF_2) or lithium fluoride (LiF) coatings are used for these passivation purposes but each has its problems. MgF_2 has an absorption cutoff at 115 nm occluding a critical part of the FUV spectrum. LiF has a lower absorption cutoff at 102.5 nm, but is hygroscopic and thus susceptible to degradation in ambient conditions. A promising alternative to these coating materials is AlF_3, which theoretically can provide reflectivity greater than 50% down to 100 nm if the coating is sufficiently thin. In this work, we explore the use of electron beam generated plasmas to simultaneously etch the native oxide layer from aluminum thin films while depositing an AlF_3 capping layer to passivate the aluminum reflector. XPS measurements indicate that this approach is cable of producing very thin (<5 nm) AlF_3 films with some mild oxygen contamination. We will discuss the impact of plasma power, chemistry, and time on the composition and structure of the passivating layer and its subsequent optical properties.________________________________* This work partially supported by the Naval Research Laboratory Base Program

TF-ThP24 Using a Semitransparent Underlayer to Determine Optical Constants of a Mostly Opaque Layer by Thin Film Interference: Application to AlF$_3$ on Al in the Extreme Ultraviolet*, **Gabriel Richardson**, K.M. Wolfe, M.D. Barona, R.S. Turley, D.D. Allred,* Brigham Young University

The presence of interference fringes in thin-film reflectance and transmission are invaluable in obtaining thicknesses and optical constants of thin-film materials. When a material is highly absorbing, however, interference fringes may not be produced. One particularly noteworthy technique to deal with this complication in and near the visible range is to place a transparent layer beneath the semitransparent thin-film whose optical properties are to be determined. (Hilfiker, et al.) A portion of the light passing through the film, reflecting off the substrate and then, transmitting again through the film, interferes with the front-surface reflected light producing interference fringes whose position depends on the layers' thicknesses and indices, and the light's wavelength and angle of incidence. The damping of the fringes also highly constrains the optical constants of the overlayer. We have extended this approach into the extreme ultraviolet to obtain the optical constants of aluminum fluoride between 17.1 and 49.5 nm using evaporated aluminum as the "transparent" interference layer. The aluminum fluoride is evaporated within minutes after the aluminum and without breaking vacuum so as to minimize the presence of oxygen on the aluminum film. The AlF3 also acts as a barrier layer, drastically retarding the oxidation of the aluminum film after it is removed from the deposition system. Complications associated with obtaining the AlF3 EUV constants include: first, the fact that the aluminum layer is not perfectly transparent, and second that, in some cases, there is an ultrathin film of aluminum oxide on the Al which formed before the barrier is deposited or forms gradually with time afterwards. In fact, it is in probing the time evolution of such oxide layer thicknesses that the technique has the promise of becoming particularly useful for studying barrier layers for broadband Al mirrors. Hilfiker, James N.; Singh, Neha; Tiwald, Tom; et al., "Survey of methods to characterize thin absorbing films with Spectroscopic Ellipsometry," THIN SOLID FILMS, 516(22), (2008) 7979-7989.

TF-ThP25 Thermoelectric Properties of Sb$_2$Te$_3$ Thin Films*, **Eshirdanya McGhee**, B. Bohara, C. Payton, S. Gere, S. Budak,* Alabama A&M University

The efficiency of the thermoelectric materials (figure of merit, ZT) that found to be limited in bulk structures has shown an enhancement by introducing nanostructures such as nanowires, multilayers, and nanocomposites. ZT relies on the Seebeck coefficient (S), the electrical conductivity (σ) and thermal conductivity (K). Nanostructure thin films have shown enhancement in ZT then bulk thermoelectric materials. DC/RF magnetron sputtering technique was utilized to fabricate nano-scale thin films of antimony telluride (Sb$_2$Te$_3$) on SiO$_2$ substrates using Sb$_2$Te$_3$ target. Thermal annealing was carried out to enhance thermoelectric efficiency by forming quantum structures within the films. The Seebeck coefficient, van der Pauw four-probe resistivity, mobility, Hall coefficient, density, measurements were performed, and power factor has been found to be improved in nano-scale thin films by thermal annealing. Thermal treatment showed positive effects on the thermoelectric properties of Sb$_2$Te$_3$ thin films on the selected temperatures. The findings will be shown during the meeting.

Acknowledgement

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TF-ThP26 Thermal Annealing Effects on the Thermoelectric Properties of CoAg Thin Films*, **Satilmis Budak**, S. Gere, E. McGhee, E. Gamble,* Alabama A&M University

Many developed countries go to the sustainable, efficient, and renewable energy sources due to the high demand in energy usage. Power generation from the thermoelectric materials is one of the promising area among the others. Efficient thermoelectric materials (TE) could convert heat into electrical energy. These materials are used as thermoelectric generators (TEG) using Seebeck effect, and thermoelectric coolers (TEC) using Peltier effect. The heat generated from TE could be used in many areas like in electrical powers, automobiles, airlines, and marine vessels. The dimensionless figure of merit, ZT, shows the efficiency of the thermoelectric materials and/or devices. ZT is calculated by multiplying the square of the Seebeck coefficient with the electrical conductivity and the temperature, then dividing it all by its thermal conductivity. DC/RF magnetron sputtering technique was used to fabricate nano-scale thin films of Cobalt-Silver (CoAg) on SiO$_2$ substrates using Co and Ag targets with co-deposition procedure. Thermal annealing was introduced to enhance thermoelectric efficiency by forming quantum structures within the films. The Seebeck coefficient, van der Pauw four-probe resistivity, mobility, Hall coefficient, density, measurements were performed, and power factor has been found to be improved in nano-scale thin films by thermal annealing. The findings will be shown during the meeting.

Acknowledgement

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, **NSF-**MRI-1337616, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

TF-ThP28 Interlayer Effect for Photocatalytic Properties of TiO$_2$/Cu$_2$O Thin Films Prepared by Reactive Sputtering*, **Akihiro Joichi**, I. Takano,* Kogakuin University, Japan

In recent years, various properties of TiO$_2$ have attracted attention and the studies have been conducted in a wide field. Particularly, in photocatalytic properties, TiO$_2$ have antifouling or antibacterial actions, and is applied to the outer wall of the building or the inner wall of the operating room. However, as the inferior point of TiO$_2$, the absorption wavelength is limited to an ultraviolet light. In the previous study, it was attempted to expand the absorption wavelength to a long wavelength by inserting a Cu$_2$O layer under a TiO$_2$ layer. On the other hand, because the photocatalytic properties of TiO$_2$ deteriorated by Cu diffusion from Cu$_2$O, a NiO layer or a TaON layer was inserted as the intermediate layer to prevent the diffusion. In this research, the effect of an inserted ZnO layer was investigated for the photocatalytic property and was compared with a NiO layer or a TaON layer.

Glass (Eagle XG) plates processed to 15 mm × 9 mm were used as substrates, and ultrasonic cleaning was performed using acetone for 5 minutes for the substrates. The multi-process coating apparatus (BC5146, ULVAC) was used to clean up the substrate by rf sputtering and to deposit the thin films of TiO$_2$, ZnO and Cu$_2$O. The deposition chamber was equipped with RF and DC sputtering cathodes. Each oxide film was formed by sputtering a Ti, a Cu or a Zn metal target in an O$_2$ atmosphere. The ultimate pressure of the deposition chamber was 8.0×10^{-6} Pa and deposition pressure was 0.08 Pa by introducing an Ar and an O$_2$ gas. Photocatalytic properties were measured by a methylene blue immersion test. In the methylene blue immersion test, a quartz cell filled by 3 ml of a methylene blue solution of 10 ppm was used and the sample immersed therein was irradiated by sterilizing light or artificial sun light for 6 hours. The chromaticity change of the methylene blue solution was measured by using a spectrophotometer at a predetermined time.

In the multi-layer thin films inserting different oxide layers, the photocatalytic measurement of the TiO$_2$/TaON/Cu$_2$O thin film showed the highest transmittance, because the optimum condition of a ZnO layer was not enough. The optimum thickness of a ZnO layer will be investigated until the conference.

TF-ThP29 The effect of Proton Radiation on ALD HfO$_2$ Films and HfO$_2$ based RRAM*, **Panpan Xue**,* University of Wisconsin-Madison*; Z. Wang,* Stanford University*; T. Chang,* University of Wisconsin-Madison*; Y. Nishi,* Stanford University*; Z. Ma, J.L. Shohet,* University of Wisconsin-Madison

The effect of proton radiation on HfO$_2$-based resistive-random-access-memory (RRAM) is investigated using 10 and 300-keV protons with fluences of 10^{13} and 10^{15} cm^{-2}. The I-V characteristics, set and reset voltage, forming process and HRS resistance were measured before and after irradiation. Each RRAM cell has a Pt/HfO$_2$/TiN metal-insulator-metal structure and a 5-nm HfO$_2$ deposited with ALD. All RRAM devices operated functionally after proton irradiation. However, a number (about 30%) of the 10-keV proton-exposed RRAM cells were formed and set to LRS after exposure. In addition, the HRS resistance exhibited a significant decrease after irradiation resulting from displacement damage. After a period of time at room temperature, the radiation-induced damage to the HfO$_2$ film recovered and the HRS resistance increased compared to the initially exposed samples. The displacement damage produces oxygen vacancies and interstitial oxygen atoms that contribute to the generation of the conductive filaments. The oxygen vacancies generated during proton irradiation at the interface can affect the forming process.

TF-ThP30 Comparison of Hafnium Oxide and Zirconium Oxide for Fabricating Electronic Devices*, **Kenneth Davis**, Z. Duncan, M. Howard, T. Wimbley, Z. Xiao,* Alabama A&M University

Thin films of hafnium dioxide (HfO_2) and zirconium oxide (ZrO_2) are used widely as the gate oxide in fabricating integrated circuits (ICs) because of their high dielectric constants. In this research, we report the growth of hafnium dioxide (HfO_2) and zirconium oxide (ZrO_2) thin film using atomic layer deposition (ALD), and the fabrication of *complementary metal-oxide semiconductor* (CMOS) integrated circuits using the HfO_2 and ZrO_2 thin films as the gate oxide. MOSFETs, CMOS inverters, and CMOS ring oscillator were fabricated, and the electrical properties of the fabricated devices were measured. The measurement results on the devices fabricated with the two films were compared, and will be reported in the Conference.

TF-ThP31 Development of the Synchrotron-based Capabilities for Direct, *In-situ* XANES/XAFS Measurements of Thermal ALD: Initial Proof-of-Concept Study Exploring ZrO_2 ALD*, **David Mandia**, B. Kucukgok, S. Letourneau, M.J. Ward, A. Yanguas-Gil, J.W. Elam,* Argonne National Laboratory

Atomic layer deposition (ALD) has become an essential tool for the design and fabrication of electronic materials key for a wide range of applications from semiconductor processing to advanced power electronics and photovoltaics. The resulting materials are characterized by thicknesses in the nm scale, they are typically amorphous and yet they exhibit unique properties that depend on growth conditions in ways that are not yet understood. As an example, ferroelectric hafnium oxide has been recently reported, achieved through the stabilization at the nanoscale of a non-centrosymmetric orthorhombic phase that is not stable at ambient pressure for bulk materials. Another example is the development of nanolaminate (NL) materials, composite thin films comprised of alternating layers of metal oxides (eg. HfO_2 and ZrO_2 in the case of ferroelectric HfO_2)that demonstrate unique optical, mechanical, and electrical properties. To this end, the stable monoclinic phase found for HfO2 has Hf-O bonds with 7-fold coordination at room temperature whereas the tetragonal phase, which is favoured for ZrO_2 at room temperature, has Zr-O bonds with an 8-fold coordination environment. The intermixing of these phases by tuning the number of ALD sub-cycles of each component – thereby changing the NL composition – can lead to non-trivial phase transformations in their local structure that deviate from their bulk composition. In this work we explore the genesis and evolution of ZrO_2 films in the first 10 ALD cycles using a custom conflat cube reactor design for *in-situ* (fluorescence mode) XANES/XAFS measurements at the Advanced Photon Source. We will present results of the direct XANES/XAFS measurement of single TDMAZr and H_2O exposures during the ZrO_2 ALD process, results of initial proof-of-principle experiments using the *in-situ* XAFS/XANESchamber and *ex-situ* XAFS/XANES results of $(HfO_2)_x(ZrO_2)_y$ NLs.

TF-ThP32 Nitridation of Transition Metal Oxide Films*, **Li Chang**, W.-L. Chen, K.A. Chiu, Y.S. Fang,* National Chiao Tung University, Hsinchu, Taiwan, Taiwan, Republic of China

Transition metal nitrides are of important industrial applications due to their good electrical conducting properties with high hardness. For formation of the nitride films, plasma nitridation of TiO_2, HfO_2 and ZrO_2 films on Si (100) substrates has been studied with microstructural characterization of x-ray diffraction, electron microscopy,and x-ray photoelectron spectroscopy. Nitriding was performed by using microwave plasma with gas mixture of nitrogen and hydrogen. It is found that microwave plasma is efficient to transform oxide into nitride from the surfaces of the oxide films. With extended nitriding time, a nitride film can be obtained on Si. Furthermore, an epitaxial nitride film can be obtained from an oxide film which was in epitaxy with Si.

TF-ThP36 Investigation of Synthesis Yield Variation of Single-Walled Carbon Nanotubes inside Horizontal Chemical Vapor Deposition Systems*, G.-H. Jeong, **Sung-Il Jo**,* Kangwon National University, Republic of Korea

Single-walled carbon nanotubes (SWNTs) have been expected to be applied to various fields such as nanoelectronic devices, transparent conducting films, energy devices and sensors due to their outstanding physical and chemical properties. A chemical vapor deposition (CVD) is the most popular method for SWNTs synthesis because of its simplicity on SWNTs synthesis process and easy control of process parameters. In general, most of the synthesis experiments have been performed in the central region of the reactor so far where temperature uniformity is guaranteed.

In this study, we report the result of detail investigation of the SWNTs synthesis yield depending on sample position in a horizontal CVD reactor. Methane and Fe thin films were used as feedstock and catalyst for SWNTs synthesis, respective ly. Ultra high resolution scanning electron microscope (UHR-SEM) was used to confirm the synthesis yield variation of SWNTs along the axial distance of the reactor. The morphology and crystallinity of the synthesized SWNTs were evaluated by atomic force microscope and Raman spectroscopy, respectively. Main result of this study shows that the highest synthesis yield of SWNTs was observed at the rear region of the reactor not the central region at all synthesis conditions. The results of this study are expected to be applicable to the synthesis of various nanomaterials using CVD process.

TF-ThP37 Optical and Mechanical Properties of Diamond-like Carbon Thin Film deposited by Filtered Cathodic Vacuum Arc Source for Durable Coating of Infrared Optics*, **Jung-Hwan In**, M.W. Seo, H.Y. Jung, S.H. Kim, J.H. Choi,* Korea Photonics Technology Institute, Republic of Korea

Diamond-like carbon (DLC) thin film is used as a durable coating in many applications (e.g. infrared optics, mold core for glass lens, engineering ceramic, cutting tool and sliding part in the engine of vehicle). DLC thin film can be categorized according to hydrogen content and sp3 bonding content [1]. Among several kinds of DLC thin film, an a-C:H thin film containing hydrogen atoms usually has been used for IR optics [2]. In this study, it was shown that tetrahedral amorphous carbon (ta-C) thin film deposited by filtered cathodic vacuum arc (FCVA) source without hydrogen addition can be used as durable coating in far and mid-IR optics. The optical transmittance in infrared and mechanical properties by using nano-indentation were measured in various substrate bias voltage conditions. The optical transmittance and hardness decreased with the substrate bias voltage. The refractive index and extinction coefficient were estimated in 1.2 µm thick ta-C coating on a Si window. The hardness of 1.2 µm thick ta-C coating measured by using nano-indentation was about 50 GPa. In addition, the effect of CH_4 gas addition in FCVA source on optical and mechanical properties of DLC coating was investigated. It was thought that a ta-C thin film by FCVA source is appropriate as a durable coating for IR optical materials with especially high elastic modulus (e.g. silicon, germanium).

Acknowledgement

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TF-ThP38 Influence of Temperature and Plasma Gas Chemistry on Atomic Layer Epitaxial Growth of InN on GaN Assessed with *In Situ* Grazing Incidence Small-Angle X-ray Scattering*, **Jeffrey Woodward**, S.G. Rosenberg,* American Society for Engineering Education (residing at U.S. Naval Research Laboratory)*; N. Nepal, S.D. Johnson,* U.S. Naval Research Laboratory*; C. Wagenbach,* Boston University*; A.C. Kozen,* American Society for Engineering Education (residing at U.S. Naval Research Laboratory)*; Z.R. Robinson,* The College at Brockport - SUNY*; D.R. Boris, S.G. Walton,* U.S. Naval Research Laboratory*; K.F. Ludwig,* Boston University*; C.R. Eddy, Jr.,* U. S. Naval Research Laboratory

Plasma-assisted atomic layer epitaxy (ALEp), a variant of atomic layer deposition in which relatively higher temperatures are utilized to promote surface diffusion for epitaxial growth, offers several potential advantages over conventional growth methods such as metalorganic chemical vapor deposition and molecular beam epitaxy for the epitaxy of III-N materials and device structures. These advantages include significantly lower growth temperatures and highly controlled layer thicknesses, the latter of which is the result of the sequential pairs of self-terminating and self-limiting reactions that constitute the growth process. However, ALEp is a relatively new method for III-N growth, and significant efforts will be required to better understand the nucleation and growth kinetics. To this end, grazing incidence small-angle X-ray scattering (GISAXS) has been previously utilized for the study of surface morphology during the ALEp growth of InN[1] and AlN[2] on a-plane Al_2O_3 substrates. GISAXS is a non-destructive technique that can probe electron density fluctuations on length scales ranging from approximately 1 nm to 250 nm in an integral manner[3], making it well-suited to the study of epitaxial growth. The resulting intensity distribution from a set of scattering objects is related to the form factor and structure factor, which are the Fourier transforms of functions describing the object shape and spatial arrangement, respectively.

In this work, we present data from *in situ* GISAXS studies performed at the Cornell High Energy Synchrotron Source during the ALEp growth of InN on bulk GaN substrates. Two growth parameters were investigated independently: temperature (180 °C, 250 °C, and 320 °C) and the ratio of N_2 to Ar gas flows into the plasma source (75/200, 31/244, and 15/260). The GISAXS patterns were analyzed in order to extract information about the evolving morphologies. The data indicate that InN islands nucleated with greater density at 180 °C than at 250 °C and 320 °C, and that the island density decreased as the growth progressed for all temperatures. While the initial areal densities and island diameters at 250 °C and 320 °C were approximately identical, the density and diameter of the latter exhibited more significant decrease and increase, respectively, with time, which may indicate a temperature-dependent coarsening due to island coalescence or Ostwald ripening. The gas flow ratio had minimal effect on diameter and density, but influenced the island shape.

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TF-ThP39 Water-based Superconcentrated Electrolytes as Gate Dielectric for High-performance Solution-processed Oxide Thin Film Transistors*, Eun Goo Lee*, *K.-H. Lim, J.T. Park, S.-E. Lee, J.H. Lee, C.I. Im, Y.S. Kim,* Seoul National University, Republic of Korea

Thin film transistors(TFTs) using oxide-based semiconductors have attracted much attention because of their large field-effect mobility, low process temperature and printing process. However, most TFTs require high operation voltage due to the low capacitance of the gate dielectric, which causes a large amount of power consumption. In order to realize electronic devices with miniaturization, light-weighting and flexibility, it is necessary to study high-k dielectrics materials which enable low operation voltage. To solve this problem, several research groups are studying various materials capable of forming an electrical double layer that lowers the operating voltage by accumulating ultra-high charge carriers at the semiconductor / dielectric interface. Herein, we propose water-based superconcentrated electrolytes films as gate dielectric materials to take advantage of the low cost, safety, environmentally friendly and high dielectric constant of water. By embedding water-based electrolytes in a cross-linking polymer network by photo irradiation, we fabricated robust and flexible free-standing films that were showed high capacitance values of 6.72 ± 0.16 uF/cm^2 at 0.5 Hz. In addition, the low electrochemical stability window of conventional aqueous electrolytes has been extended from 1.2 V to 3 V, allowing stable TFT operation at ± 1 V. The device with aqueous route indium oxide semiconductor and water-based superconcentrated electrolytes film as a dielectric layer has demonstrated an excellent electrical characteristic, including a low operating voltage (≈1 V), small subthreshold swing voltage of 110 mV/dec and the linear mobility in excess of 30.7 ± 1.6 cm^2/V s at very low drain voltage (0.1 V). These findings will open the door to the use of environmentally friendly new dielectric materials for flexible and wearable devices with low-power consumption and high mobility.

TF-ThP40 Atomic Layered Deposition and Characterizations of HfO_2 for OLED Encapsulation*, Nak-Kwan Chung,* Korea Research Institute of Standards and Science (KRISS), Republic of Korea*; S. Kim, J.Y. Yun, J.T. Kim,* Korea Research Institute of Standards and Science (KRISS)

Flexible OLED devices require encapsulation layers with low water vapor transmission rate and low temperature process. In this presentation, We report low-temperature preparation of hafnium oxides (HfO2) by atomic layer deposition (ALD). The hafnium oxide thin films were deposited from tetrakis ethylmethylamino hafnium (TEMAHf) as the Hf precursor, ozone (O3) as the reactant, and NH3 as the catalyst on 200 mm silicon wafers at substrate temperatures from 50 to 300°C. The properties of HfO2 films were investigated by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and X-ray deflection (XRD). It was found that HfO2 films grown at low temperature of 50°C using the combination of O3 and NH3 were very smooth and amorphous, and have low impurity contents.

TF-ThP41 Reaction Mechanism Study on the Atomic Layer Deposition of Titanium Oxide Film using Heteroleptic Precursors*, Jaemin Kim,* *H.-L. Kim, J. Gu, S. Kim, H. Jung, R. Hidayat, Y. Myung, W.-J. Lee,* Sejong University, Korea

Titanium oxide has been extensively studied for various applications including the high-permittivity dielectric of DRAM capacitors, photocatalysts, and optical coatings. Atomic layer deposition (ALD) technology is replacing physical vapor deposition or chemical vapor deposition to provide excellent step coverage, accurate film thickness control, and high stoichiometry film quality. The most common titanium precursors are homoleptic precursors, such as titanium tetraisopropoxide (TTIP) and tetrakis(dimethylamino)titanium (TDMAT). In general, higher deposition temperature improves the physical and electrical characteristics of the dielectric film, such as film density, stoichiometry, and purity. However, the TTIP and TDMAT decompose at over 200°C, resulting in poor step coverage and high impurity concentration. Therefore, we need titanium precursors with excellent thermal stability together with high reactivity and sufficient volatility. It was reported that mixed alkoxide-cyclopentadienyl titanium compounds show better thermal stability than titanium alkoxides, and the thermal stability is further improved by replacing $C_5H_4(CH_3)$ (MeCp) with $C_5(CH_3)_5$ (Cp*) [1]. In the present study, we investigated the reaction mechanism of ALD of titanium oxide using heteroleptic titanium precursors with different cyclopentadienyl-type ligands. $CpTi(OMe)_3$ and $Cp^*Ti(OMe)_3$ were selected to investigate the effect of cyclopentadienyl ligand. Ozone (O_3) and water (H_2O) were compared as the oxidizing agent. Saturation dose and the ALD temperature window were determined by measuring growth rates with different precursor feeding times, oxidizing agent feeding times, and the process temperatures. The surface reaction was investigated at different temperatures by using in-situ quartz crystal microbalance, in-situ Fourier transform infrared spectroscopy, and was simulated by density functional theory calculation.

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2D Materials Focus Topic
Room 201B - Session 2D+EM+MN+NS-FrM
Nanostructures including Heterostructures and Patterning of 2D Materials

Moderator: Xiang Zhang, University of California, Berkeley

8:20am **2D+EM+MN+NS-FrM1 Interfacial Strength and Surface Damage Characteristics of Two-dimensional h-BN, MoS_2 and Graphene***, **Frank DelRio**,* National Institute of Standards and Technology*; B.C. Tran Khac, K.H. Chung,* University of Ulsan, South Korea

Two-dimensional (2D) materials such as single- and multi-layer hexagonal boron nitride (h-BN), molybdenum disulfide (MoS_2), and graphene have attracted intensive interest due to their remarkable material properties. In this study, the film-to-substrate interfacial strengths and surface damage characteristics of atomically-thin h-BN, MoS_2 and graphene were systematically investigated via atomic force microscopy (AFM)-based progressive-force and constant-force scratch tests and Raman spectroscopy. The film-to-substrate interfacial strengths of these atomically-thin films were assessed based on their critical forces (*i.e.*, normal force where the film was delaminated from the substrate) as determined from progressive-force scratch tests. The evolution of surface damage with respect to normal force was further investigated using constant-force tests. The results suggested three different steps in the evolution of surface damage. At relatively low normal force, no significant change in topography and friction force was observed, which points to elastic deformation in the scratched area. As normal force increased, the formation of defects in the film and plastic deformation in the substrate were noted. At this stage, although the films have not yet failed, their topography, friction force, crystalline quality, and mechanical strengths were affected, which notably degraded their tribological performance. At normal forces above the critical force, delamination of the film from the substrate occurred. The compressive strain-induced buckling in front of the AFM tip was the primary source of mechanical instability. As the compressive strain increased, the atomic bonds were compressed, and eventually ruptured. As the number of layers increased, the tribological performance of h-BN, MoS_2, and graphene were found to significantly improve due to an increase in the interfacial strengths and a decrease in the surface damage and friction force. In all, the findings on the distinctive surface damage characteristics and general failure mechanisms are useful for the design of reliable nanoscale protective and solid-lubricant coating layers based on these 2D materials.

9:00am **2D+EM+MN+NS-FrM3 Sequential Edge-epitaxy: Towards Two-dimensional Multi-junctions Heterostructures and Superlattices***, **Humberto Rodriguez Gutierrez**,* University of South Florida **INVITED**

Atomically thin layers are known as two-dimensional (2D) materials and have attracted a growing attention due to their great potential as building blocks for a future generation of low-power and flexible 2D optoelectronic devices. Similar to the well-established 3D electronics, the development of functional 2D devices will depend on our ability to fabricate heterostructures and junctions where the optical and electronic properties of different compounds are brought together to create new functionalities. Vertical heterostructures can be produced by selective van der Waals stacking of different monolayers with distinct chemical composition. However, in-plane lateral heterostructures, where different materials are combined within a single 2D layer, have proven to be more challenging. During the formation of the hetero-junction, it is important to minimize the incorporation of undesired impurities and the formation of crystal defects at the junction that will impact the functionality of the 2D device. When fabricating periodic structures it is equally important to develop the ability to control the domain size of each material. In this talk, we will review different techniques that have been used to create 2D lateral heterostructures of transition metal dichalcogenide compounds. Emphasis will be made in our recently reported one-pot synthesis approach, using a single heterogeneous solid source, for the continuous fabrication of lateral multi-junction heterostructures of TMD monolayers. In this method, the heterojunctions are sequentially created by only changing the composition of the reactive gas environment in the presence of water vapor. This allows to selectively control the water-induced oxidation and volatilization of each transition metal precursors, as well as its nucleation on the substrate, leading to sequential edge-epitaxy of distinct TMDs. This simple method have proven to be effective for continuous growth of TMD-based multi-junction lateral heterostructures, including selenides, sulfides and ternary alloys. Basic devices with field effect transistor configuration were fabricated to study the electrical behavior of these heterojunctions, their diode-like response, photo-response as a function of laser power as well as photovoltaic behavior of the heterojunctions will be discussed.

9:40am **2D+EM+MN+NS-FrM5 Interpretation of π-band Replicas Observed for Mono- and Multi-layer Graphene Grown on 4H SiC(0001)***, T.B. Balasubramanian, M. Leandersson, J. Adell, C. Polley,* Lund University, Sweden*; **Leif Johansson**, R. Yakimova, C. Jacobi,* Linkoping University, Sweden

Graphene has made a major impact on physics due to its large variety of properties. The peculiar band structure of free standing graphene, showing linear dispersion and a Dirac point at the Fermi energy, makes it attractive for various applications. Large-scale epitaxial films have been grown on Si-terminated SiC substrates. However, the electronic structure is influenced when the graphene is laid upon a substrate whose lattice symmetry does not match that of graphene [1,2]. Six replicas oriented around each Dirac cone were observed already in the first ARPES experiments [1] of graphene grown on SiC(0001), and later reported [2] to have around 40 times lower intensity than a main Dirac cone. They were found to have the same relative separation and orientation as the rosette spots observed around the 0;th and 1x1 SiC and Graphene spots in the low energy electron diffraction (LEED) pattern and were explained [2] to have similar origin, i.e. to originate from photoelectron diffraction.

In two later ARPES investigations [3,4] additional weaker replicas were reported to exist along the Γ-K direction in the Brillouin zone of Graphene. One of them showed the existence [3] only for 1 ML but not 2 ML samples while the other reported [4] the existence in both 1 ML and 3 ML graphene samples. The origin of these replicas were in both cases attributed to a modulation of the ionic potential in the graphene layer/layers induced by the charge modulation of the carbon layer at the interface, i.e. the carbon buffer layer. Thus to an initial state effect instead of the earlier proposed final state effect. In both those experiments un-polarized HeI radiation was utilized, so the symmetry of the π-band replicas was not determined. We therefore investigated monolayer and multilayer graphene samples using linearly polarized synchrotron radiation, which allowed us to exploit the so called dark corridor [5] to directly determine the symmetry of the replica cones. Our ARPES data therefore clearly show the origin of these additional replicas observed using He-I radiation and moreover reveal the existence of some weaker replicas not earlier reported. An interpretation of our ARPES data in terms of final state photoelectron diffraction effects is shown to account for the location and symmetry of the π-band replicas observed.

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10:00am **2D+EM+MN+NS-FrM6 Effect of SiC(0001) Substrate Morphology and Termination on Multilayer Hexagonal Boron Nitride Epitaxy by Plasma-Enhanced CBE***, **Daniel J. Pennachio**, N.S. Wilson, E.C. Young, A.P. McFadden, T.L. Brown-Heft,* University of California at Santa Barbara*; K.M. Daniels, R.L. Myers-Ward, D.K. Gaskill, C.R. Eddy, Jr.,* U.S. Naval Research Laboratory*; C.J. Palmstrøm,* University of California at Santa Barbara

Despite the prevalent use of hexagonal boron nitride (hBN) in 2D devices as a gate dielectric, tunnel barrier, or substrate, the quality of hBN thin films are typically lacking relative to flakes exfoliated from bulk crystals. To address the challenges of hBN epitaxy, this work studies the growth of hBN on single-crystal epitaxial graphene on SiC(0001) via plasma-enhanced chemical beam epitaxy (PE-CBE). As PE-CBE is conducted in an ultra-high vacuum environment, hBN nucleation, composition, and morphology were able to be examined using a combination of *in-situ, in-vacuo,* and *ex-situ* characterization techniques to gain insight into the formation of high-quality hBN films and hBN/graphene heterostructures.

It was found that utilization of high growth temperature (>1400°C) and nitrogen plasma flux (5×10^{-6} Torr background pressure) resulted in improved multilayer hBN film morphology over lower temperature (1300°C) depositions and CBE growths without nitrogen plasma flux. PE-CBE also produced more stoichiometric films than CBE without plasma at temperatures above 1400°C, as determined by *in-vacuo* X-ray photoelectron spectroscopy (XPS). *In-situ* reflection high energy electron diffraction (RHEED) showed streaky diffraction patterns persisting throughout several nanometers of PE-CBE hBN growth, indicative of a smooth, epitaxial film. Crystallinity and epitaxial arrangement of hBN nuclei were examined by *in-vacuo* and *ex-situ* scanning probe microscopy (SPM). Scanning probe spectroscopy provided information on the electrical properties of the hBN films relative to bulk values.

The epitaxial alignment of the hBN/graphene/SiC(0001) heterostructure was studied by RHEED and by comparing nuclei edge alignment, as measured with SPM or scanning electron microscopy, to the substrate lattice orientation. It was found that the rotational alignment of the hBN nuclei depended on the substrate surface morphology. Nuclei on the (6√3×6√3)R30° SiC surface reconstruction, a graphene-like buffer layer, aligned directly to the buffer layer, while hBN nuclei on 4° off-cut epitaxial graphene substrates showed preferential alignment to substrate macrosteps rather than the graphene lattice. These ~25nm high macrosteps were then examined by cross-sectional transmission electron microscopy (TEM), which showed that the epitaxial graphene and hBN conformally blanketed the macrostep facets despite the macrostep's effect on nuclei orientation. The macrostep-directed nucleation outlined in this work provides a potential route to controlling the hBN/graphene rotational alignment during van der Waals epitaxy, an important variable for modulating electronic properties in this 2D system.

10:20am **2D+EM+MN+NS-FrM7 Nanoelectromechanical Drumhead Resonators from 2D Material Bimorphs***, **Sun Phil Kim**, J. Yu, E. Ertekin, A.M. van der Zande,* University of Illinois at Urbana-Champaign

Atomic membranes of monolayer 2D materials represent the ultimate limit in size of nanoelectromechanical systems. Yet, new properties and new functionality emerge by looking at the interface between layers in heterostructures of 2D materials. In this talk, we demonstrate the integration of 2D heterostructures as nanoelectromechanical systems and explore the competition between the mechanics of the ultrathin membrane and the incommensurate van der Waals interface. We fabricate electrically contacted, 5-6 µm circular drumheads of suspended heterostructure membranes of monolayer graphene on monolayer molybdenum disulfide (MoS_2), which we call a 2D bimorph. We characterize the mechanical resonance through electrostatic actuation and laser interferometry detection. The 2D bimorphs have resonance frequencies of 5-20 MHz and quality factors of 50-700, comparable to resonators from monolayer or few layer 2D materials. The frequencies and eigenmode shape of the higher harmonics display split degenerate modes showing that the 2D bimorphs behave as membranes with asymmetric tension. The devices display dynamic ranges of 44 dB, but there is a strong dependence of the dissipation on the drive. Under electrostatic frequency tuning, devices display small tuning of ~ 20% compared with graphene resonators > 100%. In addition, the tuning shows a recoverable kink that deviates from the tensioned membrane model for atomic membranes, and corresponds with a changing in stress of 0.014 N/m. One model that would account for this tuning behavior is the onset of interlayer slip in the heterostructure, allowing the tension in the membrane to relax. Using density functional theory simulations, we find that the change in stress at the kink is much larger than the energy barrier for interlayer slip of 0.0001 N/m in a 2D heterostructure, but smaller than the energy barrier for an aligned bilayer of 0.034 N/m, suggesting local pinning effect at ripples or folds in the heterostructure. Finally, we observe an asymmetry in tuning of the full width half max that does not exist in monolayer materials. These findings demonstrate a new class of NEMS from 2D heterostructures and unravel the complex interaction and impact of membrane morphology, and interlayer adhesion and slip on the mechanics of incommensurate van der Waals interfaces.

10:40am **2D+EM+MN+NS-FrM8 Atomically-precise Graphene Etch Masks for 3D Integrated Systems from 2D Material Heterostructures***, **Jangyup Son**,* University of Illinois at Urbana-Champaign*; A.M. van der Zande,* University of Illinois at Urbana Champaign

Atomically-precise fabrication methods are critical for the development of next-generation technologies in which electronic, photonic, and mechanical devices approach the atomic scale. In no area is this challenge more apparent than in nanoelectronics based on two-dimensional (2D) heterostructures, in which van der Waals (vdW) materials, such as graphene, hexagonal boron nitride (hBN), and transition metal dichalcogenides (TMDs), are integrated stacked to form functional electronic devices with nanometer thicknesses. A major challenge in the assembly of vdW heterostructure devices is the difficulty of patterning and individually connecting each molecular layer.

In this presentation, we demonstrate the use of graphene as a highly selective, atomically-thin etch mask and etch stop in van der Waals heterostructures. we also show the advantages of graphene etch masks (GEM) through advanced device demonstrations. We demonstrate that most inorganic 2D materials, such as hBN, TMDs, and black phosphorus (BP), are efficiently etched away by exposing those to XeF_2 gas at room temperature. In contrast, instead of getting etched, atomically-thin monolayer graphene is chemically functionalized (*i.e.* flurographene (FG)) under XeF_2 exposure due to the formation of sp^3 bonds by the addition of fluorine atoms onto the graphene surface. Based on this, we used exfoliated (and CVD) graphene layer as etch mask for patterning other 2D layers in micro (and macro) scale vdW heterostructures. We also demonstrate the use of this selective etching and GEM in mainly two different applications: 3D-integrated heterostructure devices with interlayer vias and suspended graphene mechanical resonators. First, we fabricate an electrical device having buried contacts in a 2D material heterostructure. Holes were etched through the top layer of hBN in an encapsulated BN-G-BN heterostructure to locally expose the buried graphene layer and contacts were fabricated by evaporating metal electrodes on the exposed graphene regions. The resulting encapsulated graphene device shows a low contact resistance of ~ 80 ohm·mm ($n = -2\times10^{12}$ cm^2) at room temperature, leading to high carrier mobility of ~ 140,000 $cm^2V^{-1}s^{-1}$, which is comparable to the electrical properties of state-of-the-art edge contacted graphene devices. Second, we fabricate a suspended graphene membrane by vapor phase etching of a BP thin film supporting graphene. We show that the graphene membrane behaves as a nanomechanical resonator with a frequency of 5.24 MHz and quality factor of ~255, comparable to graphene NEMS prepared on conventional substrates.

11:00am **2D+EM+MN+NS-FrM9 Insights into the O Atom Adsorption and O_2 Dissociation on Halogenated Graphene Surfaces***, **Reynaldo Geronia**,* University of the Philippines Diliman*; A.A.B. Padama,* University of the Philippines Los Baños, Philippines*; J.D. Ocon,* University of the Philippines Diliman, Philippines*; P.-Y. A. Chuang,* University of California, Merced

Oxygen reduction reaction (ORR) usually depends on precious metal-based catalysts like platinum and its alloys to facilitate its sluggish kinetics. The high cost of these materials however limits the employment of ORR-based technologies in commercial applications like fuel cells and metal-air batteries. Interestingly, recent works have demonstrated that doped metal-free carbon catalysts, such as graphene-based materials, can facilitate adsorption of ORR intermediate species [1]. This motivates us to investigate the interaction of oxygen atom and oxygen molecule on halogenated graphene systems.

In this work, we performed density functional theory (DFT) based calculations to investigate the stability of coplanar and non-coplanar halogen (X = F, Cl, Br, I) doped monovacant graphene systems. The stability of halogenated-graphene is strongly influenced by the size of halogen dopant as well as the geometry of the vacancy [2]. The calculated adsorption properties of atomic [3] and molecular oxygen on halogenated graphene systems, on the other hand, signifies the possibility of O_2 dissociation. We note that the dissociation of the molecule results to the distortion of the geometric structure of the substrate. This leads mostly to the formation of dangling and bridging C-O bonds along the edge of the graphene monovacancy which could have facilitated the dissociation of the molecule. Depending on the halogen, adsorption of oxygen can strengthen or weaken existing C-X bonds, due to differences between the abilities of oxygen and halogens to induce charge transfer and to participate in π bonding with carbon. These findings are expected to increase our understanding of novel graphene-based materials, which are currently being developed with the aim of reducing the use of noble metals as catalysts in fuel cells.

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Actinides and Rare Earths Focus Topic
Room 202C - Session AC+MI+SA-FrM

Actinide and Rare Earth Theory and Related Measurements

Moderators: Paul S. Bagus, University of North Texas, David Shuh, Lawrence Berkeley National Laboratory

8:20am **AC+MI+SA-FrM1 Periodic Boundary Condition and Embedded Cluster DFT Calculations of Water Adsorption on AnO_2 (An = U, Pu) Surfaces***, **Nikolas Kaltsoyannis**,* University of Manchester, UK, United Kingdom of Great Britain and Northern Ireland **INVITED**

Over half of the World's stockpile of civil plutonium (c. 126 tonnes) is stored at Sellafield in the UK as PuO_2 powder in sealed steel cans. There is evidence of gas generation in some of these cans. Many routes to gas production have been suggested, several of which involve complex, inter-connected and poorly understood PuO_2/H_2O interactions.

We have an ongoing project to study computationally the interaction of AnO_2 (An = U, Pu) surfaces with water. Standard periodic boundary condition (PBC) implementations of DFT using generalized gradient approximation (GGA) functionals can fail to reproduce key features of actinide solids, *e.g.* predicting metallic properties in systems known to be insulating. This failure stems from incorrect description of the strongly correlated 5f electrons, which are overly delocalized by the GGA, and the standard solution to this problem is to correct the GGA functionals with an onsite Coulomb repulsion term known as the Hubbard *U*. An alternative solution is to employ hybrid DFT, in which some of the exact exchange energy of Hartree–Fock theory is incorporated into the Hamiltonian. Such functionals typically produce more localized 5f electrons, and recover insulator behavior. They are, however, extremely expensive to employ in PBC calculations, and hence are rarely used. We have therefore sought a model which allows the routine use of hybrid DFT in AnO_2/water systems, and have adopted the periodic electrostatic embedded cluster method (PEECM), in which a quantum mechanically treated cluster is embedded in an infinite array of point charges. We treat a cluster of AnO_2 and adsorbing water molecules using hybrid DFT (PBE0) whilst the long-range electrostatic interactions with the bulk are modelled *via* embedding in point charges.

In this presentation, I shall describe the results of both PBC and PEECM studies of the interactions of water with both stoichiometric and reduced (oxygen vacancy) {111}, {110} and {100} surfaces of UO_2 and PuO_2. The geometries and energetics of single and multiple layers of water will be presented, together with our calculations of water desorption temperatures, from which we propose an alternative interpretation of experimental data.

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9:00am **AC+MI+SA-FrM3 Understanding the Role of Oxidation States on the Chemistry of Actinides through Integration of Theory and Experiment***, **Wibe de Jong**, J.K. Gibson,* Lawrence Berkeley National Laboratory*; R.J. Abergel,* Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

Fundamental insights into the role of 5f electrons in the redox chemistry of actinides is essential for predicting the fate and controlling the behaviour of nuclear materials in the ecosystem, as well as for developing new advanced applications in energy, medicine and forensics. In recent years computational chemistry has become a key pillar of multidisciplinary actinide research, advancing the fundamental understanding of actinide chemistry through strong synergies between experiment and simulations. We will present some recent multidisciplinary gas-phase thermochemistry and spectroscopy efforts focused on understanding the role of metal-ligand interactions on the oxidation states of actinides across the series.

9:40am **AC+MI+SA-FrM5 An Experimentalist's Viewpoint: The Tremendous Strengths and Occasional Weaknesses of Actinide Cluster Calculations***, **James G. Tobin**,* University of Wisconsin-Oshkosh

Over the course of the last several years, cluster calculations have been used in a myriad of ways to analyze spectroscopic results from actinide systems and gain insight into the electronic structure of these actinide systems. For example, the calculated 6d Unoccupied Density of States (UDOS) in Uranium Tetrafluoride and Uranium Diode were probed using U L3 (2p) X-ray Absorption Near Edge Structure (XANES) as well as U N7 (4d) X-ray Absorption Spectroscopy (XAS). [1-3] Cluster calculations have also been used successfully to study the development from atomic to bulk electronic structure in Pu [4,5] and issues associated with the 2p Occupied Density of States (ODOS) in Uranium Tetrafluoride. [6, 7] However, there now appear to be some interesting discrepancies between what has been observed experimentally and the predictions of cluster theory. In particular, the F 1s XAS of Uranium Tetrafluoride [8] and the U 4d XAS branching ratio (BR) predictions for oxidized uranium. [1] These issues will be addressed in the talk.

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10:00am **AC+MI+SA-FrM6 Ligand and Metal XAS Edges In Heavy Metal Compounds***, **Paul S. Bagus**,* University of North Texas*; C.J. Nelin,* Consultant

In previous work, [1] it has been shown that the magnitude and character of the covalent mixing in representative lanthanide and actinide oxides depends strongly on the nominal oxidation state of the oxide. In the present work, ab initio theoretical wavefunctions, WF, have been determined and have been used to obtain the energies and dipole intensities for different Near Edge X-Ray Absorption (XAS) Fine Structure, NEXAFS edges. The theoretical NEXAFS spectra have been examined in order to determine the extent to which the features of these edges can be used to infer the character and extent of the covalent bonding. An important and novel feature of the theory is that the angular momentum coupling of the open shell electrons is taken into account and the multiplets, both resolved and unresolved, associated with the various NEXAFS features are identified. Furthermore, different sets of variationally optimized orbitals are used for the initial, ground state, and the final, excited state, configurations. Thus, the relaxation and screening in response to the core-hole are taken into account. The systems examined are Ce(III) and Ce(IV) in CeO_2 and U(IV), U((V), and U(VI) in UO_x. For these systems, cation p and d edges are used to distinguish excitations to the frontier nf and (n+1)d orbitals, especially since it has been shown that both of these cation orbitals have significant covalent mixing with the ligands. The O K-edge NEXAFS is presented and the relative excitation energies and intensities into the cation nf and (n+1)d orbitals are compared to the covalent character of the different systems. The WFs are solutions of the Dirac-Coulomb Hamiltonian. [2] Comparisons are made with experiment to demonstrate the accuracy of the theoretical treatments used.

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10:40am **AC+MI+SA-FrM8 XANES Investigation into the Electronic Structure of Ce Coordination Complexes***, **Liane Moreau**, C.H. Booth,* Lawrence Berkeley National Laboratory*; Y. Qiao, E. Schelter,* University of Pennsylvania

Cerium is of particular interest among the lanthanide elements for its stability in both the Ce(III) and Ce(IV) oxidation states. This provides unique redox properties, making Ce a promising candidate for advanced energy materials. To this end, chemistries to control the Ce oxidation state have been widely developed. More interestingly, Ce-ligand bonding has in some cases shown intermediate behavior between Ce(III) and Ce(IV), which is indicative of a multiconfigurational ground state. This phenomenon results in low-energy ligand-to-metal charge transfer in addition to its magnetic behavior, such as temperature independent paramagnetism. In order to understand the effects of Ce electronic structure on compound chemical and physical properties, it is imperative to develop methods to accurately probe the fractional occupancy between 4f^1 and 4f^0 configurations.

Ce L$_3$ edge X-ray absorption near edge structure (XANES) measurements provide detailed information concerning the density of states from varying Ce-ligand bonding configurations. In particular, XANES spectra of Ce(IV) imido, Ce(III/IV) guanidinate-amide and Ce(IV) anilide complexes are presented and related to their specific coordination chemistry. From XANES, lanthanide-ligand bonding covalency is explored. We also consider the effects of varying the alkali metal species in metal-capped Ce(IV) imido. Results from the Ce(IV) complexes exhibit characteristic double white line absorption, indicative of significant 4f orbital participation in metal-ligand bonding. The extent to which covalency is observed is highly dependent on the specific ligand chemistry. In combination with DFT and magnetism results, XANES is used to study the effects of such chemistries on the orbital configurations and relate them to the observed novel properties of Ce coordination complexes.

11:20am **AC+MI+SA-FrM10 Ligand Induced Shape Transformation of Thorium Dioxide Nanocrystals***,* ***Gaoxue Wang****, E. Batista, P. Yang,* Los Alamos National Laboratory

Nanocrystals (NCs) with size and shape dependent properties are a thriving research field. Remarkable progress has been made in the controlled synthesis of NCs of stable elements in the past two decades; however, the knowledge of the NCs of actinide compounds has been considerably limited due the difficulties in handling them both experimentally and theoretically. Actinide compounds, especially actinide oxides, play a critical role in many stages of the nuclear fuel cycle. Recently, a non-aqueous surfactant assisted approach has been developed for the synthesis of actinide oxide NCs with different morphologies, but an understanding of its control factors is still missing to date. Herein we present a comprehensive study on the low index surfaces of thorium dioxide (ThO$_2$) and their interactions with relevant surfactant ligands using density functional calculations. A systematic picture on the thermodynamic stability of ThO$_2$ NCs of different sizes and shapes is obtained employing empirical models based on the calculated surface energies. It is found that bare ThO$_2$ NCs prefer the octahedral shape terminated by (111) surfaces. Oleic acid displays selective adsorption on the (110) surface, leading to the shape transformation from octahedrons to nanorods. Other ligands such as acetylacetone, oleylamine, and trioctylphosphine oxide do not modify the equilibrium shape of ThO$_2$ NCs. This work provides atomic level insights into the anisotropic growth of ThO$_2$ NCs that was recently observed in experiments, and thus may contribute to the controlled synthesis of actinide oxide NCs with well-defined size and shape for future applications.

11:40am **AC+MI+SA-FrM11 Perspectives on the Synthesis, Characterization and Applications of Upconversion and Downconversion Nanomaterials***,* ***Martin Ntwaeaborwa,*** University of the Witwatersrand, South Africa

Luminescent nanomaterials incorporating one or more active ions (usually lanthanides) have many uses today in applications such as information displays, light emitting diodes, theft prevention, advertising, medical imaging, photodynamic therapy and photovoltaic cells. In the past few decades, there has been an upsurge of research interest in the synthesis of luminescence down-conversion and up-conversion nanomaterials with different particle morphologies, and their characterization using different optical techniques. The use of lanthanide ions to convert photons either by down-conversion or up-conversion process to different and more useful wavelengths is an interesting research phenomenon for a wide range of applications. For example, the use of down-conversion and up-conversion nanomaterials to improve the power conversion efficiency of crystalline silicon solar cells and for treatment of tumour cells, respectively, have been demonstrated. While efficient down-conversion has been demonstrated from a combination of many rare-earths ions, the most efficient up-conversion has been demonstrated from only a few combination of rare-earths ions such as erbium (Er^{3+}) – ytterbium (Yb^{3+}), thulium (Tm^{3+}) – Yb^{3+}, and holium(Ho^{3+}) – Yb^{3+} incorporated in different host lattices with low phonon energies. Different mechanisms of luminescence down-conversion and up-conversion will be discussed. In addition, a few selected methods used to synthesise luminescence down-conversion and up-conversion nanomaterials will be discussed.

Biomaterial Interfaces Division
Room 101B - Session BI+AS+NS-FrM

Characterization of Biological and Biomaterial Surfaces

Moderator: Bill Theilacker, Medtronic

8:20am **BI+AS+NS-FrM1 Novel Insights into Skin Biology and Permeation of Actives using ToF-SIMS and 3D OrbiSIMS.***,* ***David Scurr,*** The University of Nottingham, UK **INVITED**

This work presents the use of mass spectrometry imaging (specifically ToF-SIMS and 3D OrbiSIMS) as an emerging tool for skin analysis, offering the ability to perform chemical histology and monitor the distribution of xenobiotic compounds, namely antibacterial, cosmetic and pharmaceutical agents. Both 2D and 3D spatial distribution profiles of analytes within skin are achievable for both topically applied compounds following permeation and inherent compounds present in native tissue. Data acquired using the 3D OrbiSIMS can identify a significant number of biological molecules, unavailable using ToF-SIMS, including subtle chemical variations within single skin strata and / or individual cells.

Individual tape stripped layers of human *stratum corneum*, both native and following application of a topical compound can be imaged using ToF-SIMS and 3D OrbiSIMS. The sensitivity of these techniques has also enabled the detection of analytes from native tape stripped samples highlighted differences in the lipid composition of the *stratum corneum* relating to both intrinsic and extrinsic aging effects[1]. In particular, a significant increase in the presence and a localised spatial distribution was observed for cholesterol sulfate, which has been shown to play a key role in desquamation.

In conducting an analysis of native *ex vivo* porcine tissue we were successfully able to detect and spatially map chemical biomarkers of both the *stratum corneum* and underlying epidermis. In addition, using a gas cluster ion beam (GCIB), the 3D distribution of analytes throughout the epidermis could be visualised for both pharmaceutical and cosmetic topical products following Franz cell experiments. These methods can be used to illustrate enhanced topical delivery, for example in the use of supramolecular gels encapsulating ascorbic acid and microneedles applied prior to the application of imiquimod used for cosmetic and pharmaceutical purposes respectively.

[1] Starr, Johnson, Wibawa, Marlow, Bell, Barrett & Scurr, *Anal. Chem*. **2016**, 88 (8), pp 4400–4408

9:00am **BI+AS+NS-FrM3 Multivariate Analysis of ToF-SIMS Data using Mass Segmented Data Matrices: Polymers and Biointerfaces***, R.M.T. Madiona,* La Trobe University, Australia*; N.G. Welch,* CSIRO Manufacturing, Australia*; D.A. Winkler,* La Trobe University, Australia*; J.A. Scoble,* CSIRO, Australia*; B.W. Muir,* CSIRO, Australia*;* ***Paul Pigram,*** La Trobe University, Australia

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is continuously advancing. The data sets now being generated are growing dramatically in complexity and size. More sophisticated data analytical tools are required urgently for the efficient and effective analysis of these large, rich data sets. Standard approaches to multivariate analysis are being customised to decrease the human and computational resources required and provide a user-friendly identification of trends and features in large ToF-SIMS datasets.

We demonstrate the generation of very large ToF-SIMS data matrices using mass segmentation of spectral data in the range 0 – 500 m/z in intervals ranging from 0.01 m/z to 1 m/z. No peaks are selected and no peak overlaps are resolved. Sets of spectra are calibrated and normalized then segmented and assembled into data matrices. Manual processing is greatly reduced and the segmentation process is universal, avoiding the need to tailor or refine peak lists for difficult sample types or variants.

ToF-SIMS data for standard polymers (PET, PTFE, PMMA and LDPE) and for a group of polyamides are used to demonstrate the efficacy of this approach. The polymer types of differing composition are discriminated to a moderate extent using PCA. PCA fails for polymers of similar composition and for data sets incorporating significant random variance.

In contrast, artificial neural networks, in the form of self organising maps (SOMs) deliver an excellent outcome in classifying and clustering different and similar polymer types and for spectra from a single polymer type generated using different primary ions. This method offers great promise for the investigation of more complex bio-oriented systems.

9:20am **BI+AS+NS-FrM4 Can you dig it? ToF-SIMS Tissue Depth Profiling***, **Daniel Graham**, T.B. Angerer, L.J. Gamble,* University of Washington

ToF-SIMS has been shown to provide detailed chemical information about cells and tissues with excellent lateral resolution. This has enabled looking at the 2D chemical distribution of lipids and other biological molecules within tissues and cells. Since cells and tissues are three dimensional constructs, it is of interest to be able to characterize their chemical composition in 3D. With the use of gas cluster ion beams (GCIBs) ToF-SIMS can attain very fine z-resolution (<10 nm) in depth profiles, however the use of ToF-SIMS for 3D imaging of biological samples is limited. This is likely due to the complexity of the materials and artifacts often encountered because of the presence of salts. In this work we use ToF-SIMS 3D depth profiling to optimize accurate reconstruction of depth profiles of planarian worm cross-sections. For this, dual beam depth profiles with a 25 keV $Bi3^+$ liquid metal ion gun (LMIG) for imaging and 10 keV Argon 1000 clusters for sputtering were acquired using an Iontof 5 system. Data reconstruction was carried out using the NBToolbox (https://www.nb.uw.edu/mvsa/nbtoolbox) ZCorrectorGui. It is well known that due to the fixed angle to of the analysis beam, the sequential images taken at each layer of the profile shift as a function of depth. Adjusting the beam steering during data acquisition and image shifting post data acquisition are used to account for this image shifting and more accurately reconstruct a 3D representation of the data. Areas with distinct structural features were chosen for depth profiles in order to aid in ascertaining the accuracy of the 3D data reconstruction. These studies will help establish the viability of 3D data reconstruction of complex biological samples and could be instrumental in being able to localize chemical distributions throughout tissues and cells.

10:00am **BI+AS+NS-FrM6 Novel Insights into Drug Release by a Functionalized Biomaterial and Dispersion into Bone using Surface Analytical Techniques***, **Marcus Rohnke**, C. Kern, B. Mogwitz, S. Ray,* Justus-Liebig University Giessen, Germany*; J. Thomas,* IFW Dresden, Germany

Bone is a complex composite material with similarities to hierarchically structured functional materials. In the case of a fracture or the need for a replacement (e.g. hip prosthesis) filler or replacement materials are necessary. Next generation bone implants are functionalised with drugs to stimulate bone healing locally or to provoke antibiotic effects. Here we focus on the release and dispersion of the anti-osteoporotic agent Sr^{2+} from strontium enriched bone cement. The knowledge of the release and dispersion kinetics of the drug plays an eminent role for the performance optimisation of the biomaterial.

Due to practical and technical reasons it is almost impossible to track the drug release kinetics, drug dispersion and the degradation of the implant material in vivo. Here we apply time of flight secondary ion mass spectrometry (ToF-SIMS) depth profiling to obtain the diffusion coefficient of Sr^{2+} in the mineralised areas of healthy and osteoporotic rat bone in post mortem examinations. For data evaluation of the depth profiles in mineralised bone we applied a simple diffusion model. The obtained diffusion coefficient for trabecular osteoporotic bone is with 1.76×10^{-10} cm^2/s more than two decades higher than that for healthy bone (2.91×10^{-12} cm^2/s). In cortical bone no significant difference in the diffusion coefficient (healthy 1.33×10^{-12} cm^2/s, osteoporotic 4.17×10^{-12} cm^2/s) could be found. The varying diffusion coefficients can be explained by the different bone nanostructure, which was investigated by focused ion beam scanning electron microscopy (FIB-SEM) and high-resolution transmission electron microscopy (HR-TEM).

The data of cement dissolution experiments into water in combination with inductively coupled plasma mass spectrometry (ICP-MS) analysis account for dissolution kinetics following Noyes-Whitney rule. For dissolution in A-MEM cell culture media the process is kinetically hindered and can be described by Korsmeyer-Peppas kinetics. An adsorbed protein layer on top of the cement surface, which was detected by ToF-SIMS, is responsible for the kinetic inhibition. Based on the results of various analytical experiments we developed a two-phase model and performed a finite element calculation for the release and dispersion of Sr^{2+} in bone. The validity of the applied model is proven by animal experiments. We compared the calculated images to mass spectrometric images of bone cross sections and achieved good conformity. It appears that drug removal via the vascular system is negligible. This is a good basis for predictions of drug mobility in bone.

10:20am **BI+AS+NS-FrM7 Spatial Distributions of Epithelial Growth Factors in Hydrogels Studied by ToF-SIMS and TIRF Microscopy for the Development of Biocompatible Multiple-protein Delivery Systems for Wound Healing***, **Shohini Sen-Britain**,* State University of New York, Buffalo*; W. Hicks,* Roswell Park Comprehensive Cancer Center*; J.A. Gardella Jr.,* State University of New York, Buffalo

This work reports the use of ToF-SIMS imaging, TIRF microscopy, and depth profiling to visualize and map the interactions of (hydroxyethyl)methacrylate (HEMA)-based hydrogels with mixtures of growth factors that are often secreted by the epithelium during wound healing. During re-epithelialization, hydrogels can act as both tissue scaffolds at the interface between healing epithelium and surrounding connective tissue, and as delivery vehicles of therapeutic proteins that expedite the wound healing process.

The spatial distribution of multiple growth factors at hydrogel surfaces can influence biocompatibility and release kinetics, orientation and conformation of the individual growth factors. Hydrogels interact with mixtures of growth factors in vivo and also when they are developed into multiple-protein delivery systems. To address these concerns, this work presents 2D and 3D spatial distributions of fluorophore-labeled growth factors varying in size, secondary structure, and hydrophobicity at the hydrogel surfaces to model the interface between porous, phase segregated drug delivery systems and complex macromolecular mixtures.

HEMA hydrogel blends incorporating methyl methacrylate (HEMA/MMA) and methacrylic acid (HEMA/MAA) cause increased hydrophobicity or hydrophilicity at the hydrogel surface, respectively. They also present phase segregation and porous topography at the surface. Depth profiling shows that smaller proteins, such as epidermal growth factor (EGF) permeate deeper into porous regions than larger proteins such as keratinocyte growth factor (KGF) and platelet-derived growth factor (PDGF). SIMS and TIRF imaging shows that proteins with more hydrophobic character such as PDGF and EGF localize at phase segregated regions containing MMA, while those with more hydrophilic character such as KGF localize at phase segregated regions containing MAA or HEMA. Biological ramifications of these results regarding biocompatibility and multiple-protein delivery systems are the focus of future work.

Magnetic Interfaces and Nanostructures Division
Room 203A - Session MI+EM-FrM

Magnetism and Spin-Orbit Coupling at Surfaces, Interfaces and Thin Films

Moderator: Valeria Lauter, Oak Ridge National Laboratory

8:20am **MI+EM-FrM1 Interfacial Spin-orbitronics: Spin-charge Current Conversion in Topological Insulators and Rashba Interfaces***, **Juan Carlos Rojas Sánchez**,* Institut Jean Lamour, Universite de Lorraine, France**INVITED**

Materials with large efficiency of spin-charge current interconversion are highly desirable to study new physical phenomena as well as for spintronics applications. Heavy metals or alloys exhibiting large spin-orbit coupling scatter the electrons in opposite directions when they have opposite spin. Thus an injection of charge current yields a transversal spin current in such materials. The charge-spin current conversion phenomenon in those 3D materials is so-called Spin Hall Effect (SHE). We can exploit this effect to manipulate a magnetization in a heavy metal/ferromagnetic structure [1-3]. We have shown such a manipulation in $Si\text{-}SiO_2$//W(3 nm)/Co_xTb_{1-x}(3.5 nm)/Al(3 nm) structures. Interesting, we have found out that the temperature of the devices reach a novel characteristic temperature just before the magnetization switching takes place [3].

On the other hand, new classes of materials such as 3D topological insulator which are trivial insulator in their bulk but hold metallic states in their surfaces are also highly interesting for spintronics. The spin-orbit coupling (SOC) in the 2DEG states at Topological Insulator (TI) or Rashba Interfaces is predicted to be more efficiency that their 3D counterparts for spin-charge current conversion. Indeed, we have found the highest efficiency at room temperature using the topological insulator α-Sn [4]. The underlying physics of charge-spin current interconversion in such 2D systems is different of the SHE and is called Edelstein Effect (EE) [5-7], also known as inverse spin galvanic effect [8]. I will show results of spin-to-charge conversion by spin pumping experiments and their analysis in term of inverse Edelstein Length [4-7] . Experimental results based on ARPES and spin pumping indicate that direct contact of metallic ferromagnetic layer is detrimental for the surfaces states of topological insulators but we can keep the surfaces states of α-Sn using Ag spacer. I will use the conversion parameters obtained at room temperature with α-Sn to demonstrate the very large advantage of the SOC effects in 2D interface states with respect to the Spin Hall Effect (SHE) of 3D metals and the resulting perspective for low power spintronic devices.

[1] M. Miron, P. Gambardella et al. Nat. **476**, 189 (2011)

[2] J.-C. Rojas-Sánchez et al. APL **108**, 082406 (2016)

[3] T. H.Pham et al. arXiv 1711.10790

[4] J.-C. Rojas-Sánchez et al. PRL **116**, 096602 (2016). ArXiv 1509.02973 (2015)

[5] J.-C. Rojas-Sánchez et al. Nat. Comm **4**, 2943 (2013)

[6] E. Lesne, J.-C. Rojas-Sánchez et al. Nat. Mat. **15**, 1261 (2016)

[7] S. Oyarzun, J.-C. Rojas-Sánchez et al. Nat. Comm. **7**, 13857 (2016)

[8] S. D. Ganichev et al. Nature **417**, 153 (2002)

9:00am **MI+EM-FrM3 Spin-orbit Coupling in Ion-surface Collisions Observed by a Polarized $^4He^+$ Ion Beam**, ***Taku Suzuki**, O. Sakai,* National Institute for Materials Science, Japan

Recently, we found spin-orbit coupling (SOC) act as a mechanism of spin dependent low-energy He^+ ion scattering on solid surfaces. It is intuitively interpreted as the effect on the projectile electron spin of the magnetic field induced by the projectile angular motion around the target nucleus during the projectile–target binary collision (Biot-Savart law). Because a polarized He+ ion beam is useful for studying surface magnetism, it is important to understand the mechanism of the spin dependent He^+ ion scattering. In the present study, we further investigated SOC from both the experimental and theoretical approaches. In the experiment, electron-spin-polarized $^4He^+$ ion beam was projected onto the target surface, and the intensity of scattered He^+ ions was measured as a function of their kinetic energy (spin-polarized ion scattering spectroscopy). We found that the scattering angle θ dependence of the spin dependent scattering is remarkably different between the targets of the transition metal and the non-transition metal. This is explained from SOC in the collisional intermediate state, in which an electron of the target is virtually transferred to the He^+ ion.

9:20am **MI+EM-FrM4 Transport and Magnetic Properties of $LaAlO_3/SrTiO_3$ Heterostructure during Cooling and Warming**, ***Zengming Zhang**, X.Q. Wang, M. Zhang, A. Rahman, R.C. Dai, Z.P. Wang, Z.J. Ding, L. Cheng,* University of Science and Technology of China

The $LaAlO_3$ thin films were grown on TiO_2 terminated (001) $SrTiO_3$ substrate using pulsed laser deposition technique. The transport and magnetic properties of $LaAlO_3/SrTiO_3$ (LAO/STO) heterostructure were studied during cooling and warming. The conductivity accelerated recoveries are found at around 70K and 160K for larger electrode interval of several mm, and more obvious for thicker LAO films. This indicated that the domain wall scale increases with the interface variation from fully strain state to partial strain state as the layers of LAO increase. During thermal cycling, both magnetoresistance(*xx*) and magnetization separate around the conductivity accelerated recovery temperature as seen in Fig. (c). The phenomenon is attributed to the mobile and trapping of defects such as single vacancy and divacancy by polarized domain walls due to the measuring current at the critical temperature [1-2].

References:

1. S. Seri *et al*, Interplay between sheet resistance increase and magnetotransport properties in $LaAlO_3$ /$SrTiO_3$, Phys. Rev. B **86**, 085118 (2012).

2. S. Seri *et al*, Thermally activated recovery of electrical conductivity in $LaAlO_3/SrTiO_3$, Phys. Rev. B **87**, 125110(2013).

9:40am **MI+EM-FrM5 Engineering the Magnetic Properties of Complex Oxide Heterostructures**, ***Yayoi Takamura**,* University of California at Davis **INVITED**

Complex oxides possess a wide range of intriguing and technologically relevant functional properties including ferromagnetism, ferroelectricity, and superconductivity. Furthermore, the interfaces of complex oxides have been shown to exhibit unexpected functional properties not found in the constituent materials. These functional properties arise due to various structural and chemical changes as well as electronic and/or magnetic interactions occurring over nanometer length scales at interfaces, and they have the potential to be harnessed to enable new, more versatile, and energy efficient devices. In this talk, I will present some of our recent work investigating the interfacial interactions which occur at ferromagnetic/antiferromagnetic (FM/AF) and FM/FM interfaces. While these interfacial interactions have been widely studied in metallic systems, fundamental differences are observed in complex oxides systems. Specifically, I will discuss FM/FM heterostructures consisting of the soft-FM $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and hard-FM $La_{0.7}Sr_{0.3}CoO_3$ (LSCO) layers which display a unique exchange spring behavior where the chemical and magnetic interfaces no longer coexist. This phenomena is explained due to the formation of an interfacial layer characterized by magnetically active Co^{2+} ions which forms due to a robust charge transfer interaction at the LSCO/LSMO interface. In the second half of the talk, I will discuss the development of measurement protocols for angle-dependent soft x-ray absorption spectroscopy measurements which can be used to unambiguously determine the orientation of the AF spin axis in (111)-oriented heterostructures and to probe how it responds to an applied magnetic field due to exchange interactions with the adjacent FM layer. For the LSMO/$La_{0.7}Sr_{0.3}FeO_3$ (LSFO) system, the LSFO layers possess two populations of AF order: the majority of AF moments cant out-of-the-plane of the film along low-index crystallographic directions, while a minority of AF moments lie within the (111)-plane. The relative orientation of the AF and FM spins differs for each type of AF domain. These results demonstrate how the many competing interactions in complex oxide heterostructures open up new opportunities to tailor their functional properties for future spintronic devices.

10:20am **MI+EM-FrM7 Location of the Valence Band Maximum in the Band Structure of Anisotropic 1T'-$ReSe_2$**, ***Markus Donath**, P. Eickholt, J. Noky,* Westfälische Wilhelms-Universität Münster, Germany*; E. Schwier, K. Shimada, K. Miyamoto, T. Okuda,* Hiroshima University, Japan*; C. Datzer, M. Drüppel, P. Krüger, M. Rohlfing,* Westfälische Wilhelms-Universität Münster, Germany

Transition-metal dichalcogenides (TMDCs) are a focus of current research due to their fascinating optical and electronic properties with possible technical applications. $ReSe_2$ is an interesting material of the TMDC family, with unique anisotropic properties originating from its distorted 1*T* structure (1*T'*). To develop a fundamental understanding of the optical and electric properties, we studied the underlying electronic structure with angle-resolved photoemission (ARPES) as well as band-structure calculations within the density functional theory (DFT)–local density approximation (LDA) and *GdW* approximations [1]. We observe anisotropic valence-band dispersions parallel to the surface. We find that along ΓM_1, which is the direction perpendicular to the "diamond" chains, the bandwidth of the hightest valence band is significantly smaller than in any other direction. Photon-energy-dependent measurements reveal a k_z-dependent band dispersion, reflecting the interlayer coupling. Two valence band maxima are identified within experimental limits of about 50 meV: one at the high-symmetry point *Z*, and a second one at a non-high-symmetry point in the Brillouin zone. Thus, the position in **k** space of the global valence band maximum is undecided experimentally. Theoretically, an indirect band gap is predicted on a DFT-LDA level, while quasiparticle corrections lead to a direct band gap at the *Z* point.

[1] P. Eickholt *et al.*, Phys. Rev. B **97**, 165130 (2018).

10:40am **MI+EM-FrM8 Controlling Antiferromagnetic Order at the Surface of La doped $BiFeO_3$**, ***Hendrik Ohldag**,* SLAC National Accelerator Laboratory*; B.-K. Jang,* Korea Advanced Institute of Science and Technology*; J.H. Lee, K-E. Kim,* Korea Advanced Institute of Science and Technology, Republic of Korea*; H. Jang,* SLAC National Accelerator Laboratory*; K.-T. Ko,* Max Planck Institute for Chemical Physics of Solids*; M.H. Jung,* Pohang University of Science and Technology, Republic of Korea*; T.Y. Koo,* Pohang Light Source*; Y.H. Jeong,* Pohang University of Science and Technology, Republic of Korea*; J.-S. Lee,* SLAC National Accelerator Laboratory*; C-H. Yang,* Korea Advanced Institute of Science and Technology, Republic of Korea

Emergence of a triple phase point in two dimensional (*e.g.* pressure and temperature) space can offer useful opportunities for the inter-coupling of two seemingly independent order parameters because of phase proximity. To illustrate the significance of this potential capability we employ a generic concept regarding electric control of magnetic order by manipulating chemical pressure: *i.e.* lanthanum substitution into the model antiferromagnetic ferroelectric $BiFeO_3$. Our results are made possible by the remarkable finding that a multiferroic triple phase point of a single spin disordered phase and two spin ordered phases emerges near room temperature in $Bi_{0.9}La_{0.1}FeO_3$ferroelectric thin films. By using spatially resolved x-ray absorption spectroscopy, we provide direct evidence that electric poling of a particular region of the compound near the triple phase point results in an antiferromagnetic phase while adjacent un-poled regions remain magnetically disordered, opening a promising avenue for magnetoelectric applications at room temperature.

11:00am **MI+EM-FrM9 Control of Magnetism at the Antiperovskite/Perovskite Interface**, *D.-F. Shao, T.R. Paudel,* ***Evgeny Tsymbal,*** University of Nebraska-Lincoln **INVITED**

Complex oxide materials with the perovskite crystal structure (ABO_3) are known for their interesting macroscopic physical properties involving the interplay between magnetism, ferroelectricity, and conductivity. Much less explored are the *antiperovskite* compounds (AXM_3) where the atomic positions of cations and anions are inverted creating unique, wide-ranging properties different from perovskites. Due to the structural similarity, interfaces combining perovskite and antiperovskite compounds can be fabricated, forming a new playground for materials design, where the coupling across the interface may lead to new fundamental properties and functional behavior. Here, based on density-functional calculations, we explore the magnetoelectric effect at the (001) interface between antiperovskite $GaNMn_3$ and perovskite $ATiO_3$ (A = Sr and Ba). Bulk $GaNMn_3$ is an antiferromagnet with the magnetic moments of the Mn ions lying in the (111) planes, forming non-collinear Γ^{5g} spin configurations with a zero net magnetization ground state. We predict that different from the Γ^{5g} non-collinear magnetism of the bulk $GaNMn_3$, strong magnetic moment enhancement and reorientation emerge at the $GaNMn_3/ATiO_3$ (001) interface, resulting in a sizable net magnetization pointing along the [110] direction. Moreover, switching the ferroelectric polarization of $BaTiO_3$ leads to reversal of the net magnetization of $GaNMn_3$. This phenomenon occurs due to the effect of ferroelectric polarization on the magnitude of the antiferromagnetic exchange coupling between the nearest Mn atoms at the interface. Reversal of magnetization by electric means is the holy grail of voltage-controlled spintronics, and thus our results pave a new route to achieve this functionality by exploiting antiperovskite/perovskite interfaces.

Nanometer-scale Science and Technology Division
Room 102B - Session NS+AM+AS+MN+PC+PS+SS+TR-FrM

SPM – Probing Chemical Reactions at the Nanoscale

Moderators: Phillip First, Georgia Institute of Technology, An-Ping Li, Oak Ridge National Laboratory

8:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM1 Using Self-Assembly to Engineer Electronic Properties in 1D and 2D Molecular Nanostructures**, ***Michael F. Crommie,*** University of California at Berkeley Physics Dept. **INVITED**

Control of chemical reactions at surfaces has created new opportunities for on-surface synthesis of low-dimensional molecular nanostructures. By designing precursor molecules it is possible to engineer new bottom-up structures with atomic precision and predetermined electronic properties. We have used this technique to confirm recent predictions that quasi-1D graphene nanoribbons (GNRs) have well-defined electronic topology. This means that when “topologically non-trivial” GNRs are fused to “topologically trivial” GNRs then a singly-occupied, topologically-protected interface state occurs at the boundary between them. This has allowed us to engineer new GNRs with unique electronic structure. We have also engineered molecular precursors to control the behavior of 2D polymers. By tuning the coupling reaction between monomers it is possible to create 2D covalent organic frameworks (COFs) that exhibit novel electronic superlattice behavior.

9:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM3 Chemical and Electronic Structure of Aniline Films on Silica Surfaces**, ***Christopher Goodwin,*** University of Delaware*; A.J. Maynes,* Virginia Polytechnic Institute and State University*; Z.E. Voras,* University of Delaware*; S.A. Tenney,* Center for Functional Nanomaterials Brookhaven National Laboratory*; T.P. Beebe,* University of Delaware

The use of silica as a substrate for polyaniline is highly appealing since silica is a common component in photovoltaics. To this end we have developed a vacuum technique for the deposition and functionalization of silica with aniline, without the need for wet chemistry. To study the chemistry of the reaction, X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS), and Atomic Force Microscopy (AFM), among other techniques, have been used. To determine the electronic structure if the resulting films, scanning tunneling microscopy and evaluation of valance band data collected by XPS was performed. By controlling the temperature of the gas-phase reaction, two states of aniline were found to exist on the silica surface. Our interest is in determining how the two states affect the electronic band structure of the surface.

9:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM4 Electric Field Driven Chemical Reaction of Individual Molecular Subunits by Scanning Tunneling Microscopy**, ***Tomasz Michnowicz,*** Max Planck Institute for Solid State Research, Germany, Deutschland*; B. Borca,* Max Planck Institute for Solid State Research, Germany*; R. Pétuya,* Donostia International Physics Centre, Spain*; M. Pristl, R. Gutzler, V. Schendel, I. Pentegov, U. Kraft, H. Klauk,* Max Planck Institute for Solid State Research, Germany*; P. Wahl,* University of St Andrews, UK*; A. Arnau,* Donostia International Physics Centre, Spain*; U. Schlickum, K. Kern,* Max Planck Institute for Solid State Research, Germany

Understanding of elementary steps and control in chemical reactions on the atomic scale might improve significantly their efficiency and applicability. Scanning tunneling microscopy (STM) allows both investigating and stimulating chemical reactions of individual organic subunits, for example via the tunneling current, electric field or a mechanical interaction. Here we present a study of an STM stimulated desulfurization process of the thiophene functional group embedded in a tetracenothiophene (TCT) molecule on a Cu(111) surface. Precise positioning and applying stimuli with the STM tip apex allows determination of a two-step process responsible for this chemical reaction. High resolution STM images, supported by the DFT calculations, help us to correlate the first reaction step to the breaking of one the carbon-sulfur bonds and the second to the breaking of the second carbon-sulfur bond. The latter reaction also results in a significant increase of the bond strength of the broken thiophene part to Cu surface atoms. The chemical reaction is triggered by positioning the tip apex above the thiophene part and applying a threshold voltage that depends linearly on the tip-molecule distance. This linear dependence is a hallmark of an electric field driven process. In addition, conduction measurements through single TCT molecules before and after the reaction have been performed. Compared to the intact molecule we observed a 50% increase of conductance after the chemical reaction, which is in agreement with the finding of a much stronger bond formation between the molecule and Cu surface atoms.

9:40am **NS+AM+AS+MN+PC+PS+SS+TR-FrM5 Characterising Conjugated Polymers for Organic Electronics by High-resolution Scanning Probe Microscopy**, ***Giovanni Costantini,*** University of Warwick, UK

The structure of a conjugated polymer and its solid-state assembly are without a doubt the most important parameters determining its properties and performance in (opto)-electronic devices. A huge amount of research has been dedicated to tuning and understanding these parameters and their implications in the basic photophysics and charge transporting behaviour. The lack of reliable high-resolution analytical techniques constitutes however a major limitation, as it hampers a better understanding of both the polymerisation process and the formation of the functional thin films used in devices.

Here, by combining vacuum electrospray deposition and high-resolution scanning tunnelling microscopy (STM) we demonstrate the ability of imaging conjugated polymers with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

Applying this novel technique to prototypical DPP- and thiophenes-containing polymers, we show that sub-molecular resolution STM images allow us to precisely identify the monomer units and the solubilising alkyl side-chains in individual polymer strands. Based on this, it becomes possible to determine the molecular number distribution of the polymer by simply counting the repeat units. More importantly, we demonstrate that we can precisely determine the nature, locate the position, and ascertain the number of defects in the polymer backbone. This unique insight into the structure of conjugated polymers is not attainable by any other existing analytical technique and represents a fundamental contribution to the long-discussed issue of defects as a possible source of trap sites. Furthermore, the analysis of our high-resolution images, also reveals that the frequently assumed all-trans-conformation of the monomers in the polymer backbone is actually not observed, while demonstrating that the main driver for backbone conformation and hence polymer microstructure is the maximization of alkyl side-chain interdigitation.

10:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM6 Probing Electrical Degradation of Lithium Ion Battery Electrodes with Nanoscale Resolution**, ***Seong Heon Kim***, Samsung Advanced Institute of Technology, Republic of Korea; *S.Y. Park, H. Jung,* Samsung Advanced Institue of Technology, Republic of Korea

The high performance of lithium-ion batteries (LIBs) is in increasing demand for a variety of applications in rapidly growing energy-related fields, including electric vehicles. To develop high-performance LIBs, it is necessary to thoroughly understand the degradation mechanism of LIB electrodes. The investigation of the electrical conductivity evolution during cycling can lead to a better understanding of the degradation mechanism in cathode and anode materials for Li-ion batteries. Here, we probed the electrical degradation of LIB electrodes with nanoscale resolution via quantitative and comparative scanning spreading resistance microscopy (SSRM). First, the electrical degradation of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) particles which are representative LIB cathode materials was studied [1]. After 300 charge/discharge cycles, stepwise-increasing resistance distributions toward the centers of the secondary particles were observed. These distributions correspond to the degenerated granular structures of the secondary particles caused by the formation of micro-cracks. Second, the electrical degradation of LIB anodes, the blended Si-C composites with graphite (Gr) particles, was investigated using SSRM [2]. From the SSRM measurements, it was obviously demonstrated that the electrical conductivity of the Si-C composite particles is considerably degraded by 300 cycles of charging and discharging, although the Gr particles maintain their conductivity. Our approach using SSRM techniques can be a good tool to study the electrical properties of various LIB electrode materials with nanoscale resolution.

[1] S.Y. Park, W.J. Baek, S.Y. Lee, J.A. Seo, Y.-S. Kang, M. Koh, S.H. Kim, Probing electrical degradation of cathode materials for lithium-ion batteries with nanoscale resolution, Nano Energy 49 (2018) 1–6.

[2] S.H. Kim, Y.S. Kim, W.J. Baek, S. Heo, D.-J. Yun, S. Han, H. Jung, Nanoscale electrical degradation of silicon-carbon composite anode materials for lithium-ion batteries, Submitted.

Plasma Science and Technology Division
Room 104A - Session PS-FrM

Plasma Modeling

Moderators: Venkattraman Ayyaswamy, University of California Merced, Premkumar Panneerchelvam, KLA-Tencor

8:20am **PS-FrM1 Investigation of Electrical Asymmetric Effect in Very High Frequency Plasma Source using Electromagnetic Plasma Model**, ***Xiaopu Li***, *K. Bera, S. Rauf, K.S. Collins,* Applied Materials

Capacitively coupled plasmas (CCP) are widely used for semiconductor material processing. One usually strives to obtain uniform fluxes of active neutrals and ions and ion energies at the substrate for optimum process uniformity. As technology is accelerating, advanced processing application requires not only uniformity but also flexible control of species fluxes and energies. Recently, electrical asymmetric effect (EAE) has been extensively studied in the literature [1-3], where separate control of ion flux and ion energy is achieved by applying a fundamental frequency and its higher harmonics in a high frequency CCP source. In the present study, EAE is systematically investigated by tailored-waveform excitations in the very high frequency (VHF) regime where electromagnetic effect becomes significant. A fully coupled electromagnetic plasma model is used to consider both EAE and electromagnetic effects. The fluid plasma model computes species densities and fluxes, as well as the plasma current density. Drift-diffusion approximation is used for species fluxes in the continuity equations for all charged species. Neutral species densities are determined by solving the continuity equations with diffusion coefficients computed using the Lennard-Jones potentials. The electromagnetic phenomena are described by the Maxwell equations with the plasma current density updated from the fluid model. The finite difference time domain (FDTD) technique is used to discretize the Maxwell equations, which are solved explicitly in time. A geometrically asymmetric discharge is excited using the VHF source and its harmonics. The phase between the excitation frequency and its harmonics has been modulated to control the electrical asymmetry. Ar discharge is studied based on the reaction mechanism similar to the previous study [4]. This study provides a fundamental understanding of EAE, that is important to achieve flexible control of ion fluxes and energies in VHF capacitively coupled plasmas.

1. U Czarnetzki *et al*, *J. Phys.: Conf. Ser.* **162** 012010 (2009)
2. E. Schüngel *et al*, *J. Appl. Phys.* **112,** 053302 (2012)
3. T Lafleur, 2016 *Plasma Sources Sci. Technol.* **25** 013001 (2016)
4. S. Rauf and M. J. Kushner, *J. Appl. Phys.* **82**, 2805 (1997)

8:40am **PS-FrM2 Simulation of Pulsed Inductively Coupled Plasmas**, ***Jun-Chieh Wang***, *W. Tian, S. Rauf, S. Sadighi, J.A. Kenney, P.J. Stout, V. Vidyarthi, J. Guo, K. Delfin, N. Lundy,* Applied Materials

Pulsed plasma processing has gained more attention lately in semiconductor industry due to its advantages over continuous wave (CW) plasmas processing. Pulsed plasma provides us with extra knobs to tailor the etching process to the desired specification, such as improved uniformity and depth loading. In this talk, a typical electronegative plasma at several mTorr with ICP source (W_s) + RF bias (W_b) of a few hundred Watts has been studied. The pulsing frequency of 1-10 KHz and duty cycle (DC) of 10% - 90% are used to investigate three pulsing schemes: source pulsing (pulsed source W_s + CW bias W_b), bias pulsing (pulsed bias W_b + CW source W_s), and their synchronized pulsing.

The plasma modeling code used in this talk, CRTRS, is a multi-dimensional hybrid plasma model. The model simultaneously solves the Poisson's equation and continuity equation for all charged species; the drift-diffusion approximation and momentum equations are solved for electron and ion fluxes. After the potential, flux and charged density have been updated, the electron energy conservation equation is solved for electron temperature. A Monte Carlo model is used to compute the ion energy and angular distribution (IEAD) at the wafer over a pulse period. The time evolution of IEAD, as well as the fluxes of relevant ions and neutral radicals at the wafer, are recorded and coupled to a 3-dimensional feature scale model for later evaluation of different pulsing modes during the Si etch step. We found that when the source power is pulsed (pulsed W_s + CW W_b), plasma extinguishes during the pulse-off period, higher sheath voltage is produced up to a few kV at lower DC as a result of lower electron density to maintain the constant W_b. When the bias power is pulsed (pulsed W_b + CW W_s), plasms density is slightly modulated by the bias power, while sheath voltage increases up to the kV level during the pulse-on period. When the source and bias powers are synchronized, IEADFs are sensitive to the phase between powers. The simulation results from plasma and feature scale model provide guidance for further experimental testing. By focusing only on the promising concepts, we are able to speed up the research cycle and gain competitive advantages.

9:00am **PS-FrM3 The Important Role of Metal Vapour in Arc Welding: New Insights from Modelling**, ***Anthony Murphy***, *J. Xiang, H. Park, F.F. Chen,* CSIRO, Australia **INVITED**

Arc welding is very widely used in manufacturing industry to join metals. The process relies on the intense heat flux from the arc plasma to partially melt metal. This also produces metal vapour, which can be transported into the arc by diffusion and convection. Metal vapour plasmas emit radiation much more strongly than those in standard welding gases such as argon and helium. The presence of metal vapour therefore leads to increased radiative cooling of the arc, which decreases the heat flux to the workpiece and leads to shallower welds.

It is well known that metal vapour dominates the arc plasma in the case of in metal inert gas / metal active gas (MIG/MAG) welding, in which the upper electrode is a metal wire whose tip melts to form droplets. Large amounts of metal vapour are produced from the wire tip, and the strong downward convective flow in the arc ensures that the central region of the arc contains around 50% metal vapour.

In contrast, the upper electrode in tungsten inert gas (TIG) welding is tungsten, which does not melt or vaporize. Metal vapour is produced only from the weld pool (the molten region of the workpiece). Computational models have predicted that the strong downward convective flow in the arc confines the metal vapour close to the workpiece. The models therefore predicted that the strong radiative cooling of the arc that is observed in MIG/MAG welding does not occur in TIG welding.

We have developed a computational model of TIG welding that treats the diffusion of the metal vapour in the arc plasma accurately for the first time. Previous treatments only considered ordinary diffusion (driven by concentration gradients); we now also take into account diffusion driven by temperature gradients and the applied electric field (cataphoresis). Our results demonstrate that cataphoresis causes upward diffusion of the metal vapour into the centre of the arc, despite the strong downward convective flow, leading to substantial radiative cooling of the arc.

We also report intriguing results obtained for TIG welding of stainless steel, in which we treat the diffusion of iron and chromium vapours separately. Our results show that the iron and chromium vapours have different trajectories through the arc, explaining the surprising measurements of Tanaka and Tsujimura (*Quart. J. Japan Weld. Soc.* **30** 164, 2012), which found that iron vapour reached only as far as the tungsten electrode tip, whereas chromium vapour was deposited on the tungsten well above its tip.

Finally, we examine the substantial influence of the choice of welding gas, arc current and other parameters on the influence of metal vapour on the arc and the weld.

9:40am **PS-FrM5 Molecular Dynamics Study on Collision Cascade Dynamics for Sputtering of Lennard-Jones Particles***, **Nicolas Mauchamp**, M. Isobe, S. Hamaguchi,* Osaka University, Japan

Plasma etching techniques have been widely used to manufacture semiconductor devices. The sizes of typical silicon (Si) based semiconductor devices are now reaching atomic sizes. The further development of plasma etching techniques to fabricate such small devices requires a better understanding of plasma-surface interactions between the material surface and impacting plasma species. Especially when the device sizes are in the range of nanometers, a high precision in plasma control is one of the key challenges for the manufacturers to obtain desired results and avoiding unwanted effects in manufactured devices. For example, during an etching process with energetic ions impacting on the material surface, surface damages caused by energetic ion bombardment may lead to the formation of non-functional regions in manufactured devices. For nanometer scale semiconductor devices, nanometer-scale plasma-induced defects in their electrically active regions typically impair the device performance. Since the last century, the interaction between a surface and an energetic incident particle as well as the collision cascade resulting from it has been widely studied, which has led to the establishment of several theories. However sputtering phenomena are highly non-linear and the system is not in thermal equilibrium, so none of these theories provides a comprehensive description of collision cascade dynamics, even for a simple case of two-body interactions such as the Lennard-Jones (LJ) interaction. In this study, as a model system, physical sputtering of a cool Lennard-Jones solid, i.e., a solid that consists of particles interacting with two-body LJ interactions and is in thermal equilibrium at a temperature sufficiently below its melting temperature, is examined with the use of Molecular Dynamics (MD) simulations. The goal of this study is to understand how the interatomic potential function of a material affects its sputtering yield, a macroscopic and non-thermodynamical property of the material. Self-sputtering of a LJ material and physical sputtering of a LJ material by the incidence of energetic non-reactive particles with different sizes and masses were examined. A non-reactive particle in this study is the one that interacts with other particles via a repulsive part of a LJ potential. From MD simulation, dependence of the sputtering yield on the normalized incident energy and the incidence angle has been obtained for different mass ratios and atomic-radius ratios between the substrate and impacting particles.

10:00am **PS-FrM6 Surface Reaction Analysis by Molecular Dynamics (MD) Simulation for SiO2 Atomic Layer Etching (ALE)***, **Satoshi Hamaguchi**, Y. Okada, M. Isobe, T. Ito, K. Karahashi,* Osaka University, Japan

Alternating application of fluorocarbon plasmas with no bias energy and Ar plasma with low bias energy to a SiO2 film is known to cause atomic layer etching (ALE) of its surface. In this ALE process, it is assumed that a thin layer of fluorocarbon is deposited on the SiO2 surface in the first step and low-energy Ar+ ion irradiation causes mixing of deposited fluorocarbon with atoms of the underlying SiO2 surface in the second step, promoting desorption of volatile SiFx and CO from the surface until fluorocarbon on the surface is completely exhausted. In this study, we have examined the surface reactions of such processes, using molecular dynamics (MD) simulations. It has been found, however, the actual surface reactions are not as simple as described above. In the Ar+ ion irradiation step, preferential sputtering of O atoms occurs even at low ion incident energy, which makes the surface more Si rich and also promotes the formation of Si-C bonds in the presence of a deposited fluorocarbon layer. In other words, in deficiency of O atoms on a SiO2 film surface, low-energy Ar+ ion irradiation may not be able to remove C atoms completely from the surface. Under such conditions, more carbon atoms may remain on the surface after each ALE cycle and etch stop may eventually occur after several ALE cycles. On the other hand, our simulation results indicate that a small amount of oxygen added to Ar+ ion irradiation may contribute to more efficient removal of carbon from the surface and also supplement the deficiency of oxygen caused by the preferential sputtering of oxygen from the surface. Simulation results are also compared with experimental observations of SiO2 ALE based on fluorocarbon plasmas.

10:20am **PS-FrM7 Atomistic Simulations of He Plasma Modification of SiO2 Thin Films for Advanced Etch Processes***, **Florian Pinzan**, R. Blanc, F. Leverd,* STMicroelectronics, France*; E. Despiau-Pujo,* 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 underlying layers of advanced nano-devices. Used as dielectric film in Flash memory devices, inter-poly Oxide-Nitride-Oxide (ONO) stack layer is directly impacted by this issue. Its bottom SiO2 layer (40Å) etching is challenging as it must be performed with nanoscale-precision in order to avoid damaging the underlayer substrate, which would lead to device performance loss. To achieve this nanometric precision etching, one possible solution may be the use of a recently developed two-step etch technology, which has already proved its worth for nitride spacers etching in terms of both anisotropy and selectivity [1]. In the first step, the material to be etched is exposed to a hydrogen (H2) or helium (He) ICP or CCP plasma; in the second step, the modified material is chemically etched by wet cleaning (HF bath) or exposure to gaseous reactants only (NH3/NF3 downstream plasmas).

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 implantation step in Si-O-N-He and Si-O-N-H systems and provide an overview of the reaction processes at the atomic scale. The objective is to understand precisely the role of the ion energy and ion dose in the implantation, and to determine the relationship between the flux/energy of plasma species (He+, Hx+, H) bombarding the surface and its structural/chemical modifications.

In this paper, we investigate specifically the interaction between low energy He+ ions and SiO2 thin films via MD simulations. We study in particular the influence of the ion energy (5-100eV) and ion dose on the substrate modification. Cumulative bombardment leads to a self-limited ion implantation followed by the formation of a modified He-implanted layer at steady state. The modified layer thickness is shown to increase with the incident ion energy, and only few sputtering of the SiO2 layer is observed in the ionic energy range considered here. Mechanisms of helium retention and desorption, as well as the detailed structure of the material at steady state, will be discussed during the presentation.

10:40am **PS-FrM8 Plasma Characteristics in a Capacitively Coupled System at Moderately High Pressure: Model and Experiment Comparison***, **David J. Peterson**, S. Shannon,* North Carolina State University*; W. Tian, P. Kraus, K. Bera, S. Rauf, T. Chua, T. Koh,* Applied Materials Inc.

Plasma parameters including electron density, effective collision frequency, effective electron temperature, voltage & current characteristics, neutral gas temperature, ion temperature and sheath thickness around the probe are measured over different pressures and powers ranging from 0.1-4.0 Torr and 20-150 W in Ar, He, Ar-He, and N_2 plasmas. Both grounded and fully floating hairpin resonator probes are used in a parallel plate capacitively coupled system driven at 27 MHz. Probe measurements are made in the axial and radial directions. Probe sheath thickness is measured using a time resolved measurement system capable of ~100 ns time resolution. Effective collision frequency is measured using the resonance full width half max. Effective electron temperature can determined from the effective collision frequency through the plasma conductivity equation but requires assuming an electron energy distribution function (EEDF). Effective electron temperatures are presented for three different EEDFs: Maxwellian, Bi-Maxwellian, and Druyvesteyn. Neutral gas temperature is measured by assuming rotational-translational equilibrium in N_2 where the second positive system is used to determine rotational temperatures. Ion temperatures are also determined through this method via the 1st negative system in N_2^+. Spatial profiles of plasma parameters along with voltage & current characteristics are compared with 2-dimensional fluid plasma simulation results. The detailed model-experiment comparison proved useful for improving understanding of plasma chemistry mechanisms in these low temperature plasmas at moderately high pressure. The possibility of inferring plasma potential from comparing floating and grounded probe measurements is discussed as well as the possibility of inferring dissociation fractions in N_2 from effective collision frequency. A new technique for manufacturing hairpin probes is discussed, which is capable of producing quality factors ~400. All analysis and data acquisition is done with open source python scripts which are freely available to the public.

11:00am **PS-FrM9 Numerical Modeling of Capacitively Coupled Plasma Process Chamber using CCPFoam***, **Abhishek Kumar Verma**[1],* University of California Merced*; K. Bera, S. Rauf,* Applied Materials*; A. Venkattraman,* University of California Merced

Plasma etching and deposition of thin films on Silicon wafers are an integral part of the microelectronics manufacturing process. To facilitate design and development of such systems, plasma modeling is of immense importance. In this work, we intend to perform computer simulations of a typical radio-frequency plasma processing system used for plasma enhanced chemical vapor deposition. Details of the rounded wafer edge and process kit geometry have been well resolved using our high performance computational framework. The 2D and representative 3D continuum simulations will be performed using widely recognized fluid model implementation in our in-house developed plasma solver library "CCPFoam" which uses robust finite volume library, OpenFOAM. The solver is capable of performing parallel multiphysics simulation using scalable algorithms and software tools for the simulation of complex physical phenomenon governed by plasma dynamics. An in-depth analysis has been performed on the usefulness and applicability of this solver in a competitive R&D work environment. Considerable emphasis is being placed on plasma modeling techniques, mainly assessing accuracy and efficiency of numerical schemes, utility of high performance numerical tools and sensitivity to input parameters. The simulations intend to show detailed analysis on the influence of physical parameters for capacitively coupled plasmas and dependence of characteristics of generated plasma on various physical parameters (e.g., process kit geometry and material properties), power supplied and operating pressure. The results will give insight into the applicability and future scope of this framework for high fidelity plasma product R&D.

11:20am **PS-FrM10 Silicon Carbide Nanoparticles for Thermoelectric Composites and Graphene Coatings for Plasmonics***, **Devin Coleman,*** University California, Riverside*; A. Hosseini, A. Greaney,* University of California, Riverside*; S. Bux, J.P. Fleurial,* Jet Propulsion Laboratory, California Institute of Technology*; L. Mangolini,* University of California, Riverside

Beta phase silicon carbide nanoparticles are produced by a two step non-thermal plasma process. The surface morphology of the particles is tunable from bare silicon carbide, and between monolayers or few-layers of graphitic or "graphene-like" shells

The bare silicon carbide particles are used as an additive for bulk n-type silicon thermoelectrics. Silicon carbide is mixed with silicon nanopowders, produced by high energy ball milling, and the composite is consolidated by conventional hot pressing into bulk pucks. 99+% density is achieved at volume fractions ranging from 0-5% silicon carbide in silicon. The addition of these nanoinclusions results in a modest decrease in both electrical and thermal conductivities. Most notably, there is also an enhancement in the magnitude of the Seebeck coefficient by up to 40%, resulting in an 80% improvement of the figure of merit, ZT, compared to the parent silicon. This effect is modeled as an energy filtering process, courtesy of Prof. Alex Greaney and his student Aria Hosseini.

The particles with graphene-like shells exhibit a broadband IR absorbance as measured by ATR-FTIR. The peak position, width, and intensity varies as a function of particle size, shell thickness, and surface coverage. A similar phenomenon has been predicted in computational work by F. Abajo for free-standing graphene structures. The computational results show narrow absorbance peaks, compared to broad features in the experimental. This is attributed to a distribution in shell size and number of layers. Additionally, Raman characterization of as-produced powders yields spectra most similar to "damaged" or "defective" graphene. A comparison of previous works, experimental results, and FDTD modeling using Lumerical software will be presented.

11:40am **PS-FrM11 Electromagnetic Effects in Wide Area Very High Frequency Linear Plasma Source***, **Kallol Bera**, X. Li, S. Rauf, K.S. Collins,* Applied Materials

Wide area very high frequency (VHF) capacitively coupled plasmas (CCP) are used for materials processing in the semiconductor and display industries. Electromagnetic effects can play significant role in plasma distributions for VHF plasma source. In this study, a VHF linear plasma source is considered, which consists of parallel conductive bars enclosed within ceramic insulator tubes. The linear source is immersed inside the discharge volume, which is enclosed by perfect conductors on the front, back, top, and bottom boundaries except for the input and output ports. Periodic boundary conditions are used on the left and right side boundaries parallel to the conductive bars in order to represent an array of conductive bars over a wide area. A full three dimensional electromagnetic plasma model is used to understand the interactions between the external radio-frequency source and the plasma. The fluid plasma model computes species densities and fluxes, as well as the plasma current density. Drift-diffusion approximation is used for species fluxes in the continuity equations for all charged species. Neutral species densities are determined by solving the continuity equations with diffusion coefficients computed using the Lennard-Jones potentials. The electromagnetic phenomena are fully described by the Maxwell equations with the plasma current density updated from the fluid model. The RF source in the model excites a transverse electromagnetic (TEM) wave through the input ports. The CPML absorbing boundary condition is applied for the termination port that avoids electromagnetic wave reflections back into the plasma. The finite difference time domain (FDTD) technique is used to discretize the Maxwell equations, which are solved explicitly in time. Ar discharge is studied based on the reaction mechanism similar to the previous study [1]. The plasma density distribution is found to be dependent on excitation frequency, pressure and power. The spatial distribution of plasma also depends on excitation phases from the ports as well as the port terminations (using either short or perfect absorption).

1. S. Rauf and M. J. Kushner, J. Appl. Phys. **82**, 2805 (1997)

12:00pm **PS-FrM12 External Circuitry Models for PIC Simulations of Cylindrical Magnetron Sputtering Chamber***, **Nate Crossette**, T.G. Jenkins, D.N. Smithe, J.R. Cary,* Tech-X Corporation

Simulations provide a means of virtually prototyping devices before building expensive physical prototypes. Virtual prototyping by means of simulation has the additional advantage of allowing rapid testing of parametric and configurational modifications. In this study, we use the highly parallelized particle-in-cell/finite-difference time-domain modeling code VSim [1] to model a 2D planar cylindrical magnetron sputtering chamber. The magnetic field of a set of permanent magnets is determined by means of a magnetostatic solver and imported into the simulation. Particle-wall interactions include sputtering and secondary electron emission. Monte Carlo interactions model collisions within the chamber. We test the effects of modifying the external circuitry on the formation of the glow discharge inside the device. We consider constant voltage and constant current circuitry. Constant current circuitry is modeled by feeding back absorbed currents from the plasma to the walls into the determination of the cathode potential. In some models we include the capacitance of the chamber, which is calculated from simulation.

1. C. Nieter and J. R. Cary, "VORPAL: a versatile plasma simulation code", J. Comp. Phys. **196**, 2004, pp. 448-473.

* Work supported by U.S. Department of Energy, SBIR Phase II award DE-SC0015762

Surface Science Division
Room 203C - Session SS+AS+HC-FrM

Near/Ambient Pressure and Bridging Gaps between Surface Science and Catalysis

Moderators: Donna Chen, University of South Carolina, Janice Reutt-Robey, University of Maryland College Park

8:20am **SS+AS+HC-FrM1 Ambient Pressure Electron Spectroscopy (XPS, XAS) and Electron Microscopy Studies of the Structure and Chemistry of Nanostructured Model Catalysts***, **John Hemminger**,* University of California Irvine **INVITED**

We use physical vapor deposition to create a high density of metal oxide nanoparticles on highly oriented pyrolytic graphite (HOPG). Photoelectrochemical methods are then utilized to selectively decorate the metal oxide nanoparticles with transition metal nanoparticles. This talk willl describe our studies of the Pt/TiO_2/HOPG ; Cu/ZnO/HOPG systems. The nanostructured surfaces are characterized by SEM, TEM, XPS, and synchrotron based XAS. Lab-based and synchrotron based ambient pressure XPS experiments have been used to study the CO oxidation reaction on Pt/TiO_2/HOPG and the CO_2 reduction reaction on

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

$CuO_x/TiO_2/HOPG$. In addition, the catalytic activity of $CuO_x/TiO_2/HOPG$ for electrochemical CO_2 reduction has been studied using differential electrochemical mass spectrometry (DEMS).

9:00am **SS+AS+HC-FrM3 *In-operando* Investigation of the Initial Oxidation Stages for NiCr-(W) Alloys with X-ray Photoelectron Spectroscopy*, Cameron Volders*,** *V. Angelici Avincola, P. Reinke,* University of Virginia

Ni-Cr alloys are of technical interest as they exhibit superior corrosion resistance due to the formation of a passive chromia film which helps protect the underlying alloy from degradation, and limits catastrophic events such as pitting and crevice corrosion. A wide range of Ni-Cr alloys have been developed to satisfy industrial needs and the properties for each alloy differ slightly based on its application. The properties are controlled by manipulating Cr content as well as adding minor alloying elements such as Mo or W, which have been shown to enhance corrosion resistance. The ideal composition for these alloys has been optimized over many decades but the mechanistic understanding of the role of Mo or W additions is not fully developed.

The current work presents an *in-operando* ambient pressure – X-ray photoelectron spectroscopy (AP-XPS) study which investigated the early stages of oxidation for four alloy concentrations; (1) Ni-5% Cr, (2) Ni-15% Cr, (3) Ni-30% Cr, and (4) Ni-15% Cr-6% W by weight percent between 573 and 773 K and $p(O_2)< 0.1$mbar. The primary objectives were to elucidate how varying Cr content in the alloys and the addition of W impacts the nucleation and growth of different oxide phases. The modulation of alloy and oxide composition and bonding was observed over an extended time period delivering a detailed view of the reaction pathways.

A key result from this work is the Cr surface segregation in the alloys prior to oxidation, which contributes to the rapid nucleation of Cr-oxides in the first reaction step with O_2. The surface enrichment of Cr influences the initial nucleation of the different oxide species and prejudices the progression of oxide growth. The main portion of this work will focus on the time evolution of the different oxide phases and the kinetics of Ni-oxide and Cr-oxide formation for all alloys, which allows to build a detailed model of the reaction. An additional component accounts for a substantial portion of the oxide signal, and is interpreted as the combination of spinel and non-stoichiometric oxide. The addition of W in the alloy resulted in a near complete suppression in the formation of Ni oxide species, and different models to interpret the impact of W on the progression of the oxidation reaction will be discussed.

9:20am **SS+AS+HC-FrM4 Surface Hydroxylation of Polar (000-1) and Non-polar (11-20) ZnO Probed with AP-XPS*, Sana Rani*,** *A. Broderick, J.T. Newberg,* University of Delaware

The interaction of ZnO with water vapor has been an important topic of research due to the relevance for numerous catalytic processes including water-gas shift reaction, methanol synthesis, olefin hydrogenation, and gas sensor applications. ZnO based humidity nanosensors were found to have high sensitivity towards humidity and fast response time in heterogeneous catalysis. The presence of water strongly modifies the surface properties depending on the substrate and coverage. The adsorbed water can catalyze heterogeneous reactions and corrosion by proton transfer and solvating products. Dissociation of adsorbed water is of particular interest for catalysis, as this may be the first step in the activation of water molecules for chemical reactions. In this work, surface thermodynamic calculations were applied to synchrotron based ambient pressure X-ray photoelectron spectroscopy (AP-XPS) data to investigate the interface between water vapor and the low index polar (000-1) and non-polar (11-20) ZnO surfaces. Three isobaric experiments were performed over a range of temperatures from 10 to 500°C. It is hypothesized that observed hydroxyl groups, adsorbed water and carbonates on the ZnO surface can significantly influence heterogeneous catalytic reactions under ambient conditions.

9:40am **SS+AS+HC-FrM5 Reason of High Stability and Reactivity of Ni/silicalite-1 Catalyst for Dry Reforming of Methane*, Evgeny Vovk*,** *X. Zhou, Z. Liu, C. Guan, Y. Yang,* ShanghaiTech University, China*; W. Kong,* Shanghai Advanced Research Institute, China*; R. Si,* Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chaina

Dry reforming of methane (DRM) is an environmentally favored process transferring two greenhouse gases (CH_4 and CO_2) into syn-gas (H_2+CO). Ni-based catalysts demonstrate good potential in this application because of comparable reactivity and low cost. DRM is highly endothermic reaction which requires high operating temperatures. At high temperatures sintering is a common issue of catalyst deactivation. Deactivation of Ni catalyst in DRM process is also accompanied by carbon deposition (coking) induced by methane decomposition and CO disproportionation (Boudouard reaction).

In the current work we investigated catalyst obtained by encapsulating Ni clusters (2.5±0.2 nm) into microporous silicalite-1 (aluminum free zeolite with MFI structure). No deactivation and coking under a wide range of conditions where carbon formation is thermodynamically favorable were observed for this sample. This atom-economical Ni/silicalite-1 catalyst was compared with Ni/SiO_2 catalyst prepared by impregnation method. XPS study has been performed in ThermoFischer ESCALAB 250X photoelectron spectrometer. The gas treatments of catalysts (up to 1 bar) was performed in high pressure gas cell (Model HPGC 300, Fermi Instruments) connected to the spectrometer.

XPS analysis of Ni/silicalite-1 demonstrates the presence of a peak with binding energy (BE) 856.2 eV in Ni $2p_{3/2}$ region. Nickel silicate has a similar spectrum shape with close BE. The presence of this peak in Ni/silicalite-1 sample suggests of the Ni-O-Si species and strong metal-support interaction. After oxidation of this sample at 400°C there are no changes of the Ni-O-Si species. At the same time nickel in Ni/SiO_2 catalyst which has shown mostly metallic Ni^0 state with minor content of Ni-O-Si upon oxidation transforms into NiO. Reduction of Ni/silicalite-1 catalyst in hydrogen at 650°C leads to partial reduction of nickel into Ni^0 while a significant portion of Ni-O-Si still remains. The behavior of Ni-O-Si feature in both oxidizing and reducing conditions clearly indicates its very high stability. We attribute this feature to the Ni-O-Si formed at the interface between Ni nanoparticles and the silicalite support. The Ni/silicalite-1 novel oxygen-philic interfacial catalyst system consists of very small metallic Ni clusters intercalated into silicalite framework and surrounded by Ni-O-Si species. Ni-O-Si provides high stability of Ni nanoparticles and prevents sintering and carbon deposition making this catalyst also very interesting for commercial application.

10:00am **SS+AS+HC-FrM6 Recent Development in XPS and Ambient Pressure XPS Techniques*, Lukasz Walczak*,** PREVAC sp. z o.o., Poland

Many important processes such as energy conversion, electrochemical, corrosion and biological processes take place at solid-gas and solid-liquid interfaces [1-3]. X-ray photoelectron spectroscopy (XPS) is the most powerful technique for understanding of these processes at the atomic level and it is the key to improving the performance of novel battery generation or renewable energy sources such as solar, wind or hydropower energy conversion devices. We would like to promote the latest equipment, technology solutions and innovations for the photoelectron spectroscopies field. Here it will be presented an innovative and compact spectrometers for the routine X-ray photoemission spectroscopy and ambient pressurephotoemission spectroscopy for study of important phenomena in the current research. The design, construction, and technical parameters of new analyser will be presented. We will report the research results of XPS measurements conducted on the photovoltaic [4], catalytical [5] or bio-materials. Moreover, it will be demonstrated the analyser operation in ambient pressure. Also the results of interaction of oxygen and surface alloy will be presented, in order to permit complete characterization for the different pressure and temperature conditions.

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10:20am **SS+AS+HC-FrM7 Quantum Mechanics and Reaction Kinetics Study on SiO_2 and SiN Dry Isotropic Chemical Etching Process*, Taiki Kato*,** *M. Matsukuma, K. Matsuzaki, L. Chen,* Tokyo Electron Technology Solutions Limited, Japan

Dry isotropic chemical etching processes are important for semiconductor manufacturing, but such processes often require subtle process tuning to achieve high etching rates and the desired etching selectivity between SiO_2 and SiN. For example, the dry chemical etching solely with HF gas (Process 1) requires fine tuning of conditions for SiN etching rate because it has a peaky dependence on the process temperature; whereas dry chemical etching with NH_3/HF binary gas mixtures (Process 2) requires subtle tuning to simultaneously maximize etching rate and SiO_2:SiN selectivity. Notably, in Process 2, SiN etching rate increases with the etching time while SiO_2 etching rate slows down with the etching time. This slowdown is attributed to the formation of an etchant diffusion barrier from the solid byproduct, AFS (Ammonium fluorosilicate). Because of these contradictions, it has been difficult to achieve highly selective and rapid SiO_2 etching, thus a better understanding of the etching mechanisms is important to further develop the high selectivity required for the formation of scaled multicomponent semiconductor device structures. This study therefore focuses on revealing these mechanisms by using the quantum mechanics and by the analysis of reaction kinetics.

Firstly, Process 1 was studied with a quantum mechanical analysis by using the GRRM (Global Reaction Route Mapping) program. For this study, GRRM searched possible etching reaction paths automatically. From this reaction path search, it was revealed that SiN etching by HF gas, when used by itself, is much more rapid than SiO_2 etching. Further analysis was conducted by the reaction kinetics analysis. The kinetics parameters comprised HF adsorption, desorption and etching reactions. This model shows good agreement with the experimental SiN etching behavior.

Moreover, Process 2 was studied with similar quantum mechanics and kinetics analyses. Quantum mechanics analysis revealed that NH_3 combined with HF enhances both SiO_2 and SiN etching reactions. An NH_4F etching model was then added to the kinetics model. Because the etching byproduct, AFS, may be both an SiN etching accelerator and an SiO_2 etching decelerator, we could model the SiN etching kinetics initiated by NH_4F and propagated by NH_4F + AFS. This model quantitatively agrees with the experimental SiN etching data. Likewise, the SiO_2 kinetics model is composed of NH_4F etching, the diffusion resistance through solid AFS and the sublimation of AFS. This model also shows good agreement with experiment.

These analyses reveal the chemical etching mechanisms and enable process optimization. Further discussion will be presented on AVS 65th.

10:40am **SS+AS+HC-FrM8 Viscosity and Surface Tension Effects on Metal Sputtered onto Low Vapor Pressure Liquids***, **Mark De Luna**, M. Gupta,* University of Southern California

Sputtering onto low vapor pressure liquids has garnered a lot of attention due to the ease of creating metal thin films and nanoparticles. However, the effects of the liquid viscosity and surface tension on the resulting morphologies has been neglected. In this work, we studied DC magnetron sputtering of gold and silver onto liquid substrates of varying viscosities and surface tensions. We were able to decouple the effects of viscosity from surface tension by depositing the metals onto silicone oils with a range of viscosities. The effects of surface tension were studied by depositing the metals onto squalene, poly(ethylene glycol), and glycerol. It was found that dispersed nanoparticles formed on liquids with low surface tension and low viscosity whereas dense films formed on liquids with low surface tension and high viscosity. We also observed that nanoparticles formed on both the liquid surface and within the bulk liquid for high surface tension liquids. Our results can be used to tailor the metal and liquid interaction to facilitate the fabrication particles and films for various applications.

Author Index

Bold page numbers indicate presenter

Author Index

Author Index

Author Index

Author Index

Author Index

Author Index

Author Index

Author Index