Atomic Scale Processing Focus Topic
Room A214 - Session AP+2D+EM+PS+TF-MoM

Area Selective Deposition and Selective-Area Patterning

Moderators: Satoshi Hamaguchi, Osaka University, Japan, Eric A. Joseph, IBM T.J. Watson Research Center

8:40am **AP+2D+EM+PS+TF-MoM2 Surface Pre-functionalization of SiN_x and SiO_2 to Enhance Selectivity in Plasma–Assisted Atomic Layer Etching**, ***Ryan Gasvoda***, Colorado School of Mines; *Z. Zhang, S. Wang, E.A. Hudson,* Lam Research Corporation; *S. Agarwal,* Colorado School of Mines

To manufacture semiconductor devices in the current sub-7-nm node, stringent processing windows are placed on all aspects in manufacturing including plasma-etching. In recent years, atomic layer etching (ALE) has emerged as a patterning technique that can provide high etch fidelity, directionality, layer–by–layer removal, and selectivity to meet the tight processing windows. Plasma–assisted ALE of SiO_2 and SiN_x is of particular interest since Si-based dielectrics are commonly used throughout the entire fabrication process. Typically, these materials are etched in a cyclic ALE process consisting of two sequential half–cycles: fluorocarbon (CF_x) deposition from a fluorocarbon plasma followed by an Ar plasma activation step. Etch selectivity can be achieved through careful manipulation of the plasma and processing parameters. To further increase overall etch selectivity, we have proposed a methodology that selectively pre–functionalizes the SiO_2 or SiN_x surface with hydrocarbons prior to ALE. Recently, we showed that an etch blocking graphitic hydrofluorocarbon film will readily accumulate on a pre–functionalized SiO_2 surface.

In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy and *in situ* 4–wavelength ellipsometry to monitor the surface reactions, film composition, and net film thickness during the entire ALE process. We show that aldehydes can be used to functionalize SiN_x with extremely high selectivity to SiO_2 surfaces. During ALE on bare SiN_x, a thick graphitic fluorocarbon film accumulates on the surface and can stop all etching after cycle 5. This is attributed to inefficient removal of both the C and N from the surface. To enhance removal and prevent graphitic carbon accumulation, we graft a branched hydrocarbon aldehyde to the SiN_x surface. This branched hydrocarbon provides an abundance of $–CH_3$ groups which allows for greater C and N removal possibly via HCN formation, thus lowering overall graphitic carbon formation. This retardation of the graphitic hydrofluorocarbon film formation leads to both an overall increase in the etch per cycle and the number of ALE cycles that can be run before an etch stop is observed.

9:00am **AP+2D+EM+PS+TF-MoM3 Area-selective Atmospheric-pressure Spatial ALD of SiO_2 using Interleaved Back-etch steps Yielding Selectivity > 10 nm**, *A. Mameli,* Holst Centre / TNO, The Netherlands; *F. Roozeboom,* ***Paul Poodt***, Holst Centre / TNO, The Netherlands, Netherlands

Area-selective atomic layer deposition (AS-ALD) has great potential in reducing cost by maskless device manufacturing of patterned layers. Still, in this new *bottom-up* approach the selectivities currently obtained for film growth on patterned growth areas vs. that on the non-growth areas are often very limited. Also the substrate throughput values for conventional low-pressure ALD is too low for industrial acceptance.(1,2) In this work we present a process for AS-ALD of SiO_2 using intermittent plasma etch-back steps to increase the selectivity above 10 nm film thickness.(3) In addition, the deposition process itself is performed in a spatial ALD reactor at atmospheric pressure which allows for achieving high throughput.(4)

AS-ALD of SiO_2 on a substrate with pre-patterned SiO_2 and ZnO areas was demonstrated using a highly chemo-selective inhibitor that chemisorbs preferentially on the non-growth area (ZnO) while allowing the deposition of SiO_2 on the growth area (SiO_2). In order to maximize the process selectivity, a blanket fluorocarbon plasma etch-back step was interleaved after every 110 ALD cycles. This way, selective SiO_2 deposition up to ~ 30 nm film thickness was demonstrated. Furthermore, X-ray Photoelectron Spectroscopy was carried out to verify the selectivity of the process: no Si was detected (detection limit 0.3 at. %) on the non-growth area, demonstrating the high selectivity of the process.

The process presented here combines selective inhibitor chemisorption, plasma-based spatial ALD with high deposition rates and plasma etch-back steps to correct for selectivity loss. This approach is compatible with *roll-to-roll* and *sheet-to-sheet* concepts and can therefore enable high-throughput AS-ALD on large-area and flexible substrates.

[1] A. Mameli, *et al.*, *ACS Nano*, **11**, 9303 (2017).

[2] F.S.M. Hashemi, *et al.*, *ACS Nano*, **9**, 8710 (2015).

[3] R. Vallat, *et al.*, *J. Vac Sc. Technol. A*, **35**, 01B104 (2017).

[4] P. Poodt, *et al.*, *Adv. Mater.*, **22**, 3564 (2010).

9:20am **AP+2D+EM+PS+TF-MoM4 Mechanisms of Precursor Blocking during Area-selective Atomic Layer Deposition using Inhibitors in ABC-type Cycles**, *M.J.M. Merkx,* Eindhoven University of Technology, The Netherlands; *D.M. Hausmann,* Lam Research Corporation; *W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands; *T.E. Sandoval,* Universidad Técnica Federico Santa María, Chile; ***Adrie Mackus***[1]*,* Eindhoven University of Technology, The Netherlands, Nederland

The development of new processes for area-selective atomic layer deposition (ALD) is currently motivated by the need for self-aligned fabrication schemes in semiconductor processing. For example, area-selective ALD processes for dielectric-on-dielectric deposition are being considered for fully self-aligned via (FSAV) fabrication schemes in advanced interconnect technology.

Instead of solely relying on surface functionalization prior to ALD, an novel strategy to area-selective ALD involves the dosing of inhibitor molecules during every cycle in an ABC-type recipe.[1,2] By using small molecules that can be dosed in vapor-phase as inhibitor, this approach is compatible with industrial process flows. Moreover, the reapplication of the inhibitor molecules during every cycle allows for the use of a plasma as the co-reactant, which broadens the range of materials that can be deposited selectively. In contrast to conventional approaches to area-selective ALD based on self-assembled monolayers (SAMs), very little is known about how small inhibitor molecules can block the ALD growth.

In this contribution, insight into the mechanisms of precursor blocking by inhibitor molecules as obtained from in-situ Fourier transform infrared spectroscopy (FTIR) and density functional theory (DFT) calculations will be discussed. Area-selective ALD of SiO_2 using acetylacetone (Hacac) as inhibitor will be described as a model system, illustrating various mechanisms that can contribute to the loss of selectivity. It was found that at saturation, Hacac adsorbs through a mixture of chelate and monodentate bonding configurations. Hacac in monodentate configuration is displaced from the surface when exposed to bis(diethylamino)silane precursor molecules, which limits the selectivity. Strategies for improving the selectivity based on the understanding from these studies will be discussed.

[1] A. Mameli, M.J.M. Merkx, B. Karasulu, F. Roozeboom, W.M.M. Kessels, and A.J.M. Mackus, ACS Nano **11**, 9303 (2017).

[2] A.J.M. Mackus, M.J.M. Merkx, and W.M.M. Kessels, Chem. Mater. **31**, 2 (2019).

9:40am **AP+2D+EM+PS+TF-MoM5 Area-Selective Deposition of TiO_2 using Isothermal Integrated Atomic Layer Deposition and Atomic Layer Etching in a Single Reaction Chamber**, ***Gregory Parsons***, *S.K. Song, H. Saare,* North Carolina State University **INVITED**

Several new approaches are emerging where chemical etching is being coupled with atomic layer deposition to achieve area-selective deposition of dielectrics and metals. During ALD, selectivity is generally lost when undesired nuclei form on the targeted non-growth surface. These undesired nuclei can sometimes be removed by periodic etching, improving the overall selectivity. However, it is not known to what extent these coupled deposition/etching sequences can proceed while maintaining good selectivity. As desirable deposition and etching reactions proceed, other changes in the process can occur to enhance unwanted nucleation and/or impede desired etching, thereby limiting the net selectivity. Recent experiments in our lab have used in-situ probes to explore coupled thermal ALD and ALE super-cycles, performed sequentially under isothermal conditions in a single reaction chamber, to achieve area selective deposition of TiO_2 on SiO_2 with hydrogen-terminated silicon (100) as the desired non-growth surface. We find that as ALD/ALE super-cycles proceed, small changes occur in the ALD and ALE reactions, particularly during the transition from ALD to ALE, or from ALE to ALD. Also, modeling studies allow us to quantitatively analyze the ASD results and compare our findings to other known approaches. These insights will be helpful to understand opportunities and challenges in advanced atomic scale reactions and process implementation.

[1] **Paul Holloway Award Winner**

10:40am **AP+2D+EM+PS+TF-MoM8 Area-Selective Atomic Layer Deposition of Metal Oxides on an Inhibitor-Functionalized SiO_2 Surface***, **Wanxing Xu**,* Colorado School of Mines*; P.C. Lemaire, K. Sharma, D.M. Hausmann,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines

The continued downscaling of modern semiconductor devices together with the incorporation of 3D architectures places new constrains on conventional lithography techniques. To enable further advances in patterning process, new techniques will be required for next-generation devices to overcome the challenges of limiting the growth of desired materials in a specific area. One method to address these issues is area-selective atomic layer deposition (ALD), which provides the opportunity to build defined patterns from the bottom-up at the atomic-level accuracy. In this study, we will focus on area-selective ALD of metal oxides including ZrO_2 and Al_2O_3 with a metal as the growth surface and inhibitor-functionalized SiO_2 as the non-growth surface. To inhibit ALD, the SiO_2 surfaces were functionalized with aminosilane inhibitors through the vapor phase or with a solution-based method. The functionalized SiO_2 surfaces were characterized by transmission Fourier transform infrared (FTIR) spectroscopy, ellipsometry, and water contact angle measurements. Metal oxides including ZrO_2 and Al_2O_3 were deposited by ALD using metal precursors and H_2O over a temperature range of 150-250 °C. *In situ* attenuated total reflection FTIR spectroscopy was utilized to identify the surface reactions sites and absorbed surface species during ALD. In addition, the corresponding film growth was measured using *in situ* four-wavelength ellipsometry.

Using *in situ* optical diagnostics, we show the mechanism for the breakdown in selectivity during area-selective ALD on a SiO_2 surface that is functionalized with aminosilanes. The infrared spectra show that aminosilane inhibitors react with almost all of the surface –SiOH groups forming Si–O–Si–R bonds on the surface (see Figure 1). After repeated exposure of the functionalized SiO_2 surface to TEMAZ and ZTB, these precursors react with Si–O–Si bonds without surface –SiOH groups (see Figure 2). Although small growth in the first few ALD cycles is not detected by *in situ* ellipsometry, growth inhibition breaks down after an increased number of ALD cycles. These results suggest that it is an additional requirement to suppress other reactions with a higher activation energy barrier during ALD expect removing main surface reactive sites through surface functionalization. To further impede growth of metal oxides on functionalized SiO_2 surface, a two-step functionalization method was developed to passivate the SiO_2 surface while providing additional steric blocking for the underlying substrates. Comparative studies were carried out to evaluate the effect of different functionalization methods on suppressing the nucleation during ALD.

11:00am **AP+2D+EM+PS+TF-MoM9 Area-selective Deposition Achieved in a Continuous Process using Competitive Adsorption***, **Taewon Suh**, Y. Yang, K.U. Lao, R.A. DiStasio, Jr., J.R. Engstrom,* Cornell University

A significant challenge for single-nm fabrication technologies is the development of area selective deposition (ASD) processes, particularly for device structures with exposed metallic and dielectric surfaces on patterned, often three dimensional, substrates. A number of techniques have been proposed and examined for ASD processes, particularly with respect to ALD, and these include the use of "permanent" blocking layers in the form of SAMs, and repetitive deposition/etch cycles. Some success has been reported with these techniques, but they possess potential drawbacks. An ideal ASD process should be fast, preferably vapor phase, and leave no residue on the non-growth surface. One technique that can possibly provide this is the use of competitive adsorption to induce area selective deposition, where a co-adsorbate is chosen that will bind much more strongly to one surface vs. another. A significant challenge concerning this approach is avoiding direct reactions between the co-adsorbate and the thin film precursor in the case of ALD, and also the co-reactant in the case of CVD. We are coupling quantum mechanical calculations of co-adsorbate/thin-film precursor/substrate interactions with experiments using our coupled micro-reactor/UHV surface analysis system. We have examined the effect of a class of unsaturated hydrocarbons as co-adsorbates on the CVD growth of ZrO_2 thin films using a Zr amido-coordination complex as the thin film precursor and O_2 as the co-reactant. The substrates were SiO_2 and Cu, and we examined the effects of both temperature, T_s = 120-240 °C, and the partial pressure of the co-adsorbate hydrocarbon. DFT calculations predict that the binding energies of these hydrocarbons are at least a factor of two larger on Cu vs. those on SiO_2. For CVD growth of ZrO_2 thin films as thick as 22 nm (growth rates of ~ 1 nm-s^{-1}), we find that the co-introduction of the hydrocarbon results in linear growth with time on a SiO_2 substrate, with no apparent incubation time, while essentially no growth is observed on Cu. *In situ*, post-deposition analysis with XPS reveals ZrO_2 thin films on SiO_2, and only adventitious carbon and less than a monolayer of Zr on the Cu surface. Consistent with a model based on competitive adsorption, we find that selectivity is eventually lost at sufficiently high substrate temperatures or sufficiently low partial pressures of the hydrocarbon co-adsorbate. Finally, we will report on the CVD growth on patterned Cu/SiO_2 substrates where we observe deposition only on those areas covered by SiO_2. We will conclude with a discussion of the promise and challenges of this approach for ASD concerning both ALD and CVD processes.

11:20am **AP+2D+EM+PS+TF-MoM10 Surface Chemistry during Plasma-Assisted ALE: What Can We Learn from ALD?***, **Sumit Agarwal**,* Colorado School of Mines **INVITED**

Due to ever decreasing device dimensions and the introduction of 3D device architectures, it is challenging to operate within a narrow processing window using conventional plasma etching. One method to address the demands of the next-generation of devices is atomic layer etching (ALE) which provides high fidelity, selectivity, and directionality, and layer-by-layer removal. Plasma-assisted ALE has been extensively studied for a variety of materials, including Al_2O_3, HfO_2, Si, and Si–based dielectrics. Plasma-assisted ALE of SiO_2 or SiN_x typically uses two sequential steps in a cyclic fashion: CF_x deposition from a C_4F_8/Ar plasma followed by an Ar plasma activation step. However, the surface chemistry during plasma ALE is not well understood. In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy and *in situ* four-wavelength ellipsometry during ALE to monitor the surface reactions, film composition, as well as the net film thickness. Similar to area-selective atomic layer deposition, we show that surface functionalization prior to ALE can be used to alter the etch per cycle. Using this methodology, I will discuss how selective functionalization of SiO_2 or SiN_x can be used to alter the selectivity during plasma-assisted ALE.

Plasma Science and Technology Division
Room B131 - Session PS1+SE-MoM

Atmospheric-Pressure Plasmas

Moderators: Michael Gordon, University of California at Santa Barbara, François Reniers, Université Libre de Bruxelles, Belgium

8:20am **PS1+SE-MoM1 On the Versatility of Atmospheric Non-equilibrium Plasmas: Material Synthesis, Packaging Sanitation and Oncological Applications***, **Matteo Gherardi**, V. Colombo, F. Barletta, A. Bisag, C. Bucci, F. Capelli, R. Laurita,* Alma Mater Studiorum-University of Bologna, Italy*; E. Mezzofanti,* AlmaPlasma srl*; T. Gallingani,* Alma Mater Studiorum-University of Bologna, Italy, Italia*; G. Girolimetti, S. Coluccelli, L. Amato, G. Gasparre,* S.Orsola-Malpighi Hospital, Bologna, Italy*; M. Perrone,* S. Orsola-Malpighi Hospital, Bologna, Italy*; A.M. Porcelli,* Alma Mater Studiorum-University of Bologna, Italy*; P. De Iaco,* S. Orsola-Malpighi Hospital, Bologna, Italy **INVITED**

Non-equilibrium atmospheric pressure plasmas (APPs) are an extremely versatile sources of reactive species, UV radiation, radicals and electrons, showing the promise of new medical therapies and offering innovative means to induce chemical reactions and synthesize materials. Trying to capture the versatility of this technology and to depict the current challenges, the presentation will deal with three different technological applications of APPs.

In the first part of the talk, APP biocidal potential is discussed in the industrial perspective of producers of food/beverage packaging and packaging machines. In this field, a fast and economic packaging sanitation is required in order to guarantee a sufficient shelf life to the product. Advantages and limitations of APPs with respect to conventional technologies, as well as the challenges of scaling plasma equipment up to the dimensions required by the industrial production volumes will be discussed.

In the second part of the talk, recent findings on the oncological applications of APPs will be presented. The discussion will focus in particular on Epithelial Ovarian Cancer (EOC), the fifth leading cause of cancer-related death among women and a disease characterised by the diffusion of nodules or plaques from the ovary to the peritoneal surfaces (carcinosis), with a poor prognosis at diagnosis (15-20% within 5 years) in advanced stages (III-IV). Due to the limitations of the currently available therapeutic options, the use of APPs is envisioned to produce plasma

activated liquids (PALs) containing reactive oxygen and nitrogen species (RONS) to wash the intraperitoneal cavity with the aim of selectively provoking apoptosis in cancer cells without damaging the healthy ones.

Finally, the use of APPs for the synthesis of materials will be discussed in the frame of the development of an innovative multi-layer coating able to reduce biofilm proliferation onto a biomedical device, while at the same time preserving its bio- and hemo-compatibility, avoiding blood clots formation. An APP assisted process is here used to deposit all the different layers of the coating, composed by silver nanoparticles (AgNPs) embedded in a plasma polymerized HMDSO (ppHMDSO) matrix. The coating characteristics will be discussed in light of the results provided by chemo-morphological analysis and cellular and anti-biofilm assays.

9:40am **PS1+SE-MoM5 Streamers Effects in Cold Atmospheric Plasma Applications: Coatings, Gas Conversion, Surface Chemistries***, A. Ozkan, J. Mertens,* ***François Reniers,*** Université Libre de Bruxelles, Belgium

For a long time, research in atmospheric plasma dielectric barrier discharges (DBDs) focused on homogeneous discharges. However, most of the DBDs present inhomogeneities in the form of streamers.

In this presentation, we aim at showing the drastic effect of these streamers on the chemical reactivity of the discharges. Consequences can be found for instance on the chemistry and on the roughness of plasma deposited coatings, on the deposition rates, or on the conversion of gases inside the discharge. These streamers can be studied through a high speed/high sensitivity camera, and by recording the current – voltage curves with a Rogowski coil on an oscilloscope. The chemistry in the plasma phase is studied using mass spectrometry, optical emission spectroscopy and gas chromatography. Roughness can be measured using profilometry or AFM, and the surface chemistry is analyzed by XPS.

The effect of the streamers will be demonstrated using the following examples :

- the plasma polymerization of CFx coatings, in Argon or Helium leads to different coatings chemistriess and roughnesses, induced by the streamers. This leads to coatings with contact angle varying from 110° (PTFE like) to more than 140°.

- the plasma polymerization of anhydrides shows that the number of streamers depends on the nature of the anhydride injected, and more specifically on the presence of double bonds, and their location. This affects the final chemistry of the coatings, but also the deposition rate.

- the conversion of CO_2 by a DBD is a highly filamentary discharge. Although this is due to the electronegative nature of CO_2, we show that, by changing the dielectric, and by playing with the plasma parameters, one can significantly vary the number of streamers. We also show that this number of streamers seems to be a key factor for the gas conversion.

10:00am **PS1+SE-MoM6 Improved Water Intrusion Resistance on Adhesive Bonded Metals using Atmospheric CVD SiO_2 Barrier Coatings***,* ***Zachary Jeckell,*** *D. Patel, T. Choi, M. Schmid, L. Bónová, D.E. Barlaz, D.N. Ruzic,* University of Illinois at Urbana-Champaign*; I.A. Shchelkanov, B.E. Jurczyk,* Starfire Industries LLC

Lightweight manufacturing, specifically the bonding of dissimilar metals is gaining traction lately as the automobile industry looks for new ways to reduce the weight of their vehicles without compromising the safety or performance. However, current technologies such as spot welding can either be difficult, as is the case for aluminum and magnesium, or impossible as is the case for carbon fiber reinforced polymers. The Center for Plasma Material Interactions (CPMI) has developed a scalable method for performing atmospheric plasma enhanced chemical vapor deposition (AP-CVD) using a 2.45 GHz microwave power supply and a torch design that allows for inline precursor delivery to the plasma. Atmospheric plasmas offer unique advantages for manufacturing, such as the potential to be directly integrated into an assembly line, as well as the ability to deposit on complex geometries. This research investigates the feasibility of depositing SiO2, using hexamethyldisiloxane (HMDSO) as the chemical precursor, onto materials commonly used in lightweight manufacturing and then applying an automotive adhesive to bond the materials together. The silica layer is intended to function as both an adhesion promoter as well as a water barrier coating. The composition of the film is verified using XPS, and the film morphology and thickness are observed using cross-sectional SEM to verify that the deposited film is dense and in the range of 10-100 nm. The robustness of these films is determined by adhesion testing following deposition of silica, as well as after water soak testing which are used to simulate prolonged exposure to realistic environments. Preliminary water soak testing on aluminum has shown a decrease in max stress of 2.5% after 168 hours of water soak at 55 °C, which is a significant improvement over the 25% benchmark currently used in the automotive industry.

10:40am **PS1+SE-MoM8 OES Imaging and Double Langmuir Probe Studies of Flow-through, Supersonic Microplasma Jet Sources***, K.E. Mackie,* ***Michael Gordon,*** University of California at Santa Barbara

Spatially-resolved OES imaging and double Langmuir probe (DLP) measurements were carried out on flow-through supersonic microplasma jets to highlight how plasma operating conditions (e.g., pressure, current, presence of growth precursors/O_2, distance from the nozzle) affect the local gas (T_{rot} and T_{trans}) and electron (T_e) temperatures in the plasma jet plume. T_{rot} and T_{vib} were estimated using semi-empirical and rigorous quantum mechanical fits to OES spectra of the first positive group of N_2 ($B^3\Pi$ --> $A^3\Sigma_u^+$), and T_e was obtained via fits to DLP IV curves. Experiments on Ar jets with downstream pressures in the 10-200 Torr regime yielded estimates of $T_{rot} = T_g$ and T_{vib} of 500-700 K and 5000-6000 K, respectively, using two independent methods. DLP data gave estimates of T_e in the 1-3 eV range, which depended on the exact location in the expanding jet plume. The transition between a pre-discharge-like operating regime at low plasma currents to true hollow cathode operation at high currents was also observed in the plasma IV characteristic and companion OES measurements. The talk will highlight OES imaging and DLP results, as well as the effect of gas additives, i.e., the presence of film deposition precursors and/or oxidants in the jet feed vs. background gas, on jet operating characteristics (T_e, T_{gas}, etc.).

11:00am **PS1+SE-MoM9 Time-resolved Optical Emission Spectroscopy of an Atmospheric Pressure Plasma Jet – Surface Interaction***,* ***Michael Johnson,*** *D.R. Boris, Tz.B. Petrova, S.G. Walton,* U.S. Naval Research Laboratory

Atmospheric pressure plasma jets (APPJs) have become a valuable tool for the modification of surfaces. One of the large benefits of APPJs is their ability to generate a chemically-rich environment in open air, allowing for the modification of a board range of surfaces including metals, polymers, ceramics, and biological materials. However, when an APPJ interacts with a surface, the surface will influence the structure of the plasma jet and thereby alter the chemistry of the jet. This is particularly vital because different chemical species important for surface modification will form in different quantities depending on the surface. Because of this, two different surfaces treated by the same plasma jet will undergo exposure to slightly different conditions. In this work, time-resolved measurements of the optical emission of a pulsed-DC plasma jet impinging on different surface is measured to investigate how the structure and chemistry of the plasma on the surface evolve in time. Initially, the plasma source emits a streamer which propagates out from the jet nozzle into the open air and eventually collides the surface. With a metal surface, a 'secondary stroke' forms on the surface and extends back towards the jet outlet. The formation, extension, and duration of the stroke are functions of the pulse width and frequency of the voltage waveform used to generate the plasma jet. The metal surface allows for the formation of a long-lived, surface plasma that exists for the duration of the pulse. If a dielectric surface is impinged with the APPJ, the streamer will strike the surface and produces an ionization wave that extends along the surface. The ionization wave is short-lived and not significantly affected by the length of the pulse. This work is supported by the Naval Research Laboratory base program.

11:20am **PS1+SE-MoM10 Atmospheric-Pressure Plasmas As Ionization Sources For Atomic, Molecular, And Biological Mass Spectrometry***,* ***Jacob Shelley,*** *S. Badal, C. Walton, G. MacLean,* Rensselaer Polytechnic Institute*; I. Ayodeji,* University of South Florida*; G. Chan,* Lawrence Berkeley National Laboratory*; T. Evans-Nguyen,* University of South Florida **INVITED**

Analytical plasmas that operate at ambient pressures and mass spectrometry (MS) have been in a symbiotic relationship since the near-coincident advent of the inductively coupled plasma (ICP) ionization source and atmospheric-pressure (AP) inlets for mass spectrometers. Preceding that discovery by only a few years, it was shown that low-power plasmas could be used for soft ionization of intact molecules through chemical ionization pathways. More recently, analytical plasma source development has seen a resurgence with the realization of a variety of low-power AP plasma designs useful as MS ionization sources. AP plasmas are unique in that they have the ability to create a wide-range of energetic species useful for desorption and/or ionization processes.

Plasmas produce highly energetic species (e.g., ions, metastable neutrals, fast electrons, etc.), which can lead to high-energy physical or chemical processes to fragment and ionize molecules. This fragmentation can be so extensive that molecules are broken down into bare elemental

constituents. In addition, low-energy ionization reactions can also occur due to the abundance of collisional cooling that can take place at ambient pressures. For instance, the helium-based flowing atmospheric-pressure afterglow (FAPA) source has been shown to produce intact molecular ions of molecular species with quite high ionization efficiencies.

This presentation will demonstrate the broad utility and range of applications of low-power AP glow discharges, specifically the FAPA discharge, and the solution-cathode glow discharge (SCGD). The possibilities of these devices extend well beyond conventional atomic and small molecule detection. By tuning the chemistry of the discharge, we can alter conventional ionization modes to encompass elemental analysis to biomolecular detection to polymer analysis. For instance, our group has developed a method to detect elemental ions with FAPA-MS via online complexation reactions with volatile ligands. But, the open-air nature of FAPA can produce isobaric interferences from ambient species. To overcome this issue, differential mobility spectrometry was used as a post-ionization filter to remove background ions. Ultimately, FAPA-DMS may dramatically improve selectivity and sensitivity in fieldable MS applications. Meanwhile, it was found that SCGD-MS could be used for the detection of atomic, molecular, and biological species directly from solutions. Furthermore, it was found that peptides could be tunably fragmented at atmospheric pressure, which led to 100% sequence coverage for many of the peptides examined.

Plasma Science and Technology Division
Room B130 - Session PS2-MoM

Plasma Modeling

Moderators: Mingmei Wang, TEL Technology Center, America, LLC, Nathan Marchack, IBM T.J. Watson Research Center

8:20am **PS2-MoM1 Computational Modeling of Capacitively Coupled Plasmas at Moderate Pressures in gases of Argon, Helium and Nitrogen***, **Wei Tian**,* Applied Materials*; D. Peterson, S.C. Shannon,* North Carolina State University*; S. Rauf,* Applied Materials

Shrinking features and 3D structures in integrated circuits are pushing the semiconductor manufacturing processes to a new level of complexity. Processes that combine etching and deposition steps including rapid cycling between them have become important to achieve the desired features and structures. A plasma source design which enables etching and deposition in the same chamber is desirable. In this paper, we report on a computational investigation of capacitively coupled plasmas in the same reactor with pressure ranging from 0.1 Torr to 4.0 Torr in Ar, He and N_2, respectively. The pressure range covers typical etching and deposition conditions. Spatio-temporal profiles of plasma properties along with voltage and current characteristics are compared with experimental results. In this reactor, the plasma is formed in the gap between the top powered electrode and bottom grounded electrode. Electron density peaks at the chamber center at lower pressure, < 0.5 Torr, and becomes concentrated near the top edge when pressure is increased. In He plasma, electrons are produced mainly through electron impact ionization at lower pressure; at higher pressure, Penning ionization starts to dominate. In Ar plasma, electron impact ionization always dominates electron production due to lower Ar ionization threshold. Both in He and Ar plasma, the rf voltage decreases with the pressure. In contrast to the atomic gases, the N_2 plasma exhibits a more localized plasma density profile. The rf voltage does not monotonically change with the pressure. The rf voltage decreases from 0.1 Torr to 0.75 Torr in N_2 plasma and increases with higher pressure.

8:40am **PS2-MoM2 Relation between Atomic Interaction Parameters of a Surface Material and its Physical Sputtering Yield; How to Predict the Etching Rate based on the Surface Material Properties***, **Nicolas Mauchamp**, M. Isobe, S. Hamaguchi,* Osaka University, Japan

Since the invention of a transistor in the last century, the typical dimensions of semiconductor devices have diminished and are now reaching the atomic sizes. Plasma etching techniques have been widely used to manufacture semiconductor devices. However, as the device dimensions decrease and a wider variety of materials are used to form highly advanced devices, the precise control of device structures during the etching process has become extremely challenging. A better understanding of plasma-surface interactions during the etching process is expected to help one obtain the desired device structures and avoid unwanted effects such as damage formation during the etching processes. Plasma-surface interaction with surface chemical reactions and collision cascade due to energetic ion impact have been widely studied both experimentally and theoretically. Such interaction should be determined from atomic interactions among atoms and ions involved in the process, so that once the material properties of the surface and physical properties of incident ions and radicals are known, macroscopic surface reaction properties such as the etching rate and resulting surface chemical compositions should be predictable. However, the relation between such atomic properties and macroscopic process parameters are so complex that few (empirical) formulas exist that relate material properties and process properties (e.g., etching rate) and are valid under wide process conditions.

In this study, we consider a Lennard-Jones (LJ) solid, which is an FCC crystalline solid made of particles interacting through a simple two-body LJ potential function, and analyze its physical sputtering properties using Molecular Dynamics (MD) simulation. The goal of this study is to understand the dependency of the physical sputtering yield, a macroscopic and non-thermodynamic property of the material, on the interatomic potential functions [1]. In this presentation, we focus our discussion on the sputtering yields at high incident ion energies, where the sputtering yield depends sensitively on the repulsive potential of the surface atoms and incident ions. We also compare the simulation results with experimental sputtering yield data archived in Ref. [2], in an attempt to relate thermodynamical properties of the surface material and atomic properties of incident ions to the observed sputtering yield, based on an analogy to the sputtering properties of the LJ system that we analyze in detail in this study.

[1]N. A. Mauchamp, et al., AVS 65th International Symposium and Exhibition, PS-FrM05 (2018).

[2]Y. Yamamura and H. Tawara, Atomic Data and Nuclear Data Tables 62, 149-253 (1996).

9:00am **PS2-MoM3 Investigation on the Uniformity Control of the Electron and the Ion Kinetics in a Capacitively Coupled Plasma Reactor using a Parallelized Particle-in-Cell Simulation***, **Hae June Lee**,* Pusan National University, Republic of Korea*; H.J. Kim,* Dong A Uiversity, Republic of Korea*; J.S. Kim,* Tokyo Electron Technology Solutions Limited, Japan **INVITED**

The radially non-uniform power absorption in a capacitively coupled plasma (CCP) causes non-uniform plasma density and temperature which results in the spatial variations of etching or deposition profiles. In this study, we investigate the electron energy probability function (EEPF) in the bulk plasma and the ion energy and angle distribution function (IEADF) on the substrate using a two-dimensional particle-in-cell simulation. The spatial variation of the EEPFs and the IEADFs are observed with the variation of the electrode structure and the gas pressure. The non-uniform transition of the heating mode from stochastic heating to Ohmic heating was observed to be enhanced with the side wall effect in CCP deposition reactors. While the ionization rate is affected by the heating mode transition and the electron density, the IEADFs are mainly affected by the time-average potential profiles for a single high-frequency CCP. However, the dual frequency CCP has more variety for the control of the IEADF uniformity.

9:40am **PS2-MoM5 Capacitively Coupled Plasma Uniformity Improvement Using Phase and Amplitude Control of Electrode Potential***, **Xiaopu Li**, K. Bera, S. Rauf,* Applied Materials

Capacitively coupled plasmas (CCPs) are widely used for semiconductor material processing to provide uniform active neutral and ion fluxes and their energies that lead to on-wafer process uniformity. High density discharge at Very High Frequency (VHF) is required to produce enough reactive radicals for Plasma Enhanced- Chemical Vapor Deposition (PE-CVD), Atomic Layer Deposition (PE-ALD) and Atomic Layer Etching (PE-ALE). However, the uniformity of discharge profile is strongly affected by both electrostatic coupling and electromagnetic standing wave effects that depend on reactor design and operating conditions. Consequently, it is challenging to achieve adequate on-wafer uniformity using high-density discharge that utilizes high power density. Electric potential modulation has been proposed for the uniformity control of VHF CCPs using external circuits [1], and separate power sources [2]. In the present work, a compact size reactor is modeled with parallel plate electrodes and grounded chamber walls at moderately high pressure driven by power in kWs. The amplitudes and phases of electrode potentials are modulated by external circuits or two separate power sources. The discharge profile is systematically investigated by a fluid-based plasma model using Ar discharge [3]. This study demonstrates a tunable plasma profile using

phase and amplitude control of electrode potential, which is important to achieve flexible uniformity control in high-density VHF CCPs.

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10:00am **PS2-MoM6 Kinetic Modeling of Non-Equilibrium Plasmas for Modern Applications**, ***Igor Kaganovich***, *A. Khrabrov, A. Powis,* Princeton Plasma Physics Laboratory

We have studied several non-equilibrium plasma devices where kinetic effects determine plasma self-organization: neutralization of ion beams and electron cloud effects in accelerators, negative hydrogen Ion Sources, ExB discharges (plasma switch and Penning discharge), thermoelectric converters.

Neutralization of positive ion beam space-charge by electrons is important for many accelerator applications, i.e., heavy ion inertial fusion, and ion beam-based surface engineering. Past experimental studies showed poorer ion beam neutralization by electron-emitting filaments, compared with neutralization by plasmas. Now researchers have found that reduced neutralization may be related to the generation of electrostatic solitary waves (ESWs) during the neutralization process, as the ion beam passes through the electron-emitting filaments. [1].

We have also developed a Global Model Code for Negative Hydrogen Ion Sources, GMNIS [2]. The codes ultimate goal is to aid developing optimized negative ion beams for ITER. The code solves volume-averaged equations: continuity for plasma species and electron energy equation for the electron temperature, and include more than 1000 volumetric and surface reactions for interactions of electrons, ground-state atomic and molecular hydrogen, molecular ions and atomic ions, negative ions, 14 vibrationally-excited states of molecular hydrogen, and excited atoms. Results of the code are benchmarked against another code [2]. Convenient analytical solution for vibrational spectrum of H_2 was also derived.

We have studied the low-pressure (left-hand) branch of the Paschen curve at very high voltage when electrons are in the runaway regime and charge exchange/ionization avalanche by ions and fast neutral atoms becomes important for plasma switch application, which operates at 100-500KV range. For these voltages, a multi valued Pashen curve was observed. We performed particle-in-cell simulations and developed analytical model that can explain experimentally observed Pashen curve .[3]

We have also preformed studies of rotating spoke in a Penning discharge and proposed analytical scaling law for its frequency [4].

Efficient thermal electric converter is proposed in Ref.[5].

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10:40am **PS2-MoM8 Automated Reduction of Plasma Chemistry Sets**, ***Sebastian Mohr,*** Quantemol Ltd., UK; *M. Hanicinec,* University College London, UK; *A. Dzarasova,* Quantemol Ltd., UK; *J. Tennyson,* University College London, UK

Simulating plasma reactors in multi-gas mixtures easily leads to chemistry sets comprising dozens of species and many hundreds of reactions. Including such complex chemistry sets in spatially resolved plasma models quickly becomes infeasible due to the high computational cost. Hence, it is desirable to keep a chemistry set simple while preserving the behavior of the plasma with regards to the density etc. of key species such as the radicals interacting with the surface. We are developing an algorithm within the Quantemol Database (QDB) [1] to automate this simplification for specified process parameters such as pressure, power, and gas mixture [2]. The algorithm will select a minimum set of species and reactions from the entirety of the database, which produce the same results with regards to user-specified species and the desired accuracy.

The challenge here is to find a reduction method, which can be automated reliably with minimum human input and is computationally cheap enough to run within the QDB framework. One method, which satisfies the need for quick calculation times is to run a 0D model with the full set of reactions and species, identify species with negligible densities, and remove these and associated reactions from the chemistry set. This requires only one run of the 0D model and a check of the species densities with the set threshold density. However, there are a few pitfalls concerning reliable automation. For example, a specie might have a low density in the steady state solution but act as a precursor for a more numerous specie, which would be missed by such an algorithm.

On the other side of the spectrum is the Morris method [3] based on Monte Carlo techniques. Here, the rate coefficients for the specific reactions are randomly changed for each run of the model. The effect of each reaction on the plasma system can be evaluated by the perturbations of, for example, densities of specified species caused by the variation in the rate coefficients. Reactions with low impact can be removed as well as species whose reactions showed no significant effect. This method is much more reliable without additional human input but requires a large number of simulation runs to gather enough data. Hence, it might be unfeasible to be used within the QDB infrastructure.

Given this, we require a method between these two extremes. Here, we will present our assessment of different methods, the current stage of development, and examples for chemistry reduction for specific process parameters.

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11:00am **PS2-MoM9 Prediction of Etch Rates for New Materials by Machine Learning - Case Study for Physical Sputtering**, ***Kazumasa Ikuse,*** Osaka University, Japan; *H. Kino,* National Institute for Materials Science (NIMS), Japan; *S. Hamaguchi,* Osaka University, Japan

Due to the latest development of new chip designs, various non-conventional materials, such as ferromagnetic metals for magnetoresistive random access memories (MRAMs) and perovskite-type oxides for resistive random access memories (ReRAMs), have been introduced to microelectronics devices and required to be processed together with conventional Si based materials in the chip manufacturing processes. Furthermore, as the device dimensions are approaching the atomic scale, new process technologies, such as atomic-layer deposition (ALD) and atomic-layer etching (ALE), have been introduced to the surface processing, where the interactions between the processed surface and newly introduced gaseous species are not necessarily well understood. Having a variety of choices for surface materials and process conditions increases the complexity of process development because of our insufficient knowledge on surface reactions in the new processes. With a large number of possible choices of process conditions, exhaustive search for process optimization by experiments is prohibitively expensive. One of the possible solutions to this problem is to use machine learning (ML) to predict certain characteristics of the surface reactions such as the etching/deposition rates and surface chemical compositions, based on the existing knowledge of materials and gas-phase molecules involved in the new processes.

As the first step to develop such technologies based on data driven science, we have developed a system to predict the physical sputtering yields of single-element materials under single-species ion bombardment [1,2], based on the experimental sputtering yield data provided in Ref. [3]. Identification of the material/ion properties, which we call “descriptors,” that the sputtering yield strongly depends on is the key for the successful prediction of sputtering yields under unknown conditions. In this study, the selection of descriptors was performed by the sparse modeling with the exhaustive search method [4] and the subgroup relevance method [5].

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11:20am **PS2-MoM10 Maskless and Contactless Patterned Silicon Deposition using a Localized PECVD Process**, ***Ronan Leal**, B. Bruneau, P. Bulkin, T. Novikova, F. Silva,* LPICM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, France; *N. Habka,* TOTAL GRP - New Energies, France; *E.V. Johnson,* LPICM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, France

We present a novel technique to perform contactless and mask-free patterned plasma enhanced chemical vapor deposition (PECVD) and etching. When a powered electrode with narrow slits is placed very close to the substrate, plasma is selectively ignited within the slits due to the hollow cathode effect, and so deposition or etching occurs only within an area smaller than the size of the slit. This technique is demonstrated through the deposition of hydrogenated amorphous silicon using a gas mixture of hydrogen and silane. Slits as small as 1 mm generate a plasma, and for this width, the lines deposited are about 750 µm wide, homogenous over their length (60 mm), and are deposited at a rate of 50 nm/min. The phenomenon is studied using Particle In Cell (PIC) modelling. The electron localization observed in the PIC modelling provides an explanation of why the deposition is narrower than the slit. In addition, an excellent correlation between results of modeled ion flux profile and experimental etching profile is observed.

This technique offers several advantages as it allows the lithographic function to be performed (i) directly, including for high quality semiconductor layers that can be deposited using PECVD, and (ii) in a contactless fashion, as the technique does not require a mask to be in contact with the substrate, (iii) at high rates without depositing powder, and (iv) in a reactor chamber that can be also used to deposit homogenous blanket layers simply by backing the electrode away from the surface.

Thin Films Division
Room A122-123 - Session TF+EM+MI+MN+OX+PS-MoM

Functional Thin Films: Ferroelectric, Multiferroics, and Magnetic Materials

Moderators: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, France, Jessica Kachian, Intel Corporation

8:20am **TF+EM+MI+MN+OX+PS-MoM1 A Room-Temperature Magnetoelectric Multiferroic made by Thin Film Alchemy**, *D.G. Schlom,* ***Megan Holtz**,* Cornell University **INVITED**

Materials that couple strong ferroelectric and ferromagnetic order hold tremendous promise for next-generation memory devices. Meticulous engineering has produced novel ferroelectric and multiferroic materials, although known single-phase multiferroics remain limited by antiferromagnetic or weak ferromagnetic alignments, by a lack of coupling between the order parameters, or by having properties that emerge only well below room temperature. Here we construct single-phase multiferroic materials in which ferroelectricity and strong magnetic ordering are coupled near room temperature. Starting with hexagonal $LuFeO_3$—a geometric ferroelectric with planar rumpling—we introduce individual monolayers of ferrimagnetic $LuFe_2O_4$ within the $LuFeO_3$ matrix, that is, $(LuFeO_3)_m/(LuFe_2O_4)_1$ superlattices. The rumpling of the $LuFeO_3$ drives the ferrimagnetic $LuFe_2O_4$ into a ferroelectric state, reducing the $LuFe_2O_4$ spin frustration. This increases the magnetic transition temperature to 281K for *m*=9. Moreover, the ferroelectric order couples to the ferrimagnetism, enabling direct electric-field control of magnetism at 200 kelvin. Further, charged ferroelectric domain walls align at $LuFe_2O_4$ layers, resulting in charge transfer which increases the magnetic moment. We are currently pursuing higher temperature multiferroics by incorporating cubic spinels with high magnetic ordering temperatures, such as $CoFe_2O_4$, into the $LuFeO_3$ matrix. Our results demonstrate a design methodology for creating higher-temperature magnetoelectric multiferroics through epitaxial engineering.

9:00am **TF+EM+MI+MN+OX+PS-MoM3 Magnetic Losses in FeGa/NiFe/Al_2O_3 Laminates for Strain-Mediated Multiferroic Micro-Antenna Applications**, ***Kevin Fitzell**, A. Acosta, C.R. Rementer, D.J. Schneider, Z. Yao,* University of California, Los Angeles; *C. Dong,* Northeastern University; *M.E. Jamer, D. Gopman, J. Borchers, B. Kirby,* National Institute of Standards and Technology (NIST); *N. Sun,* Northeastern University; *Y. Wang, G.P. Carman, 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 material with strong magnetoelastic coupling and acceptable magnetic losses at high frequency.

Galfenol ($Fe_{84}Ga_{16}$ or FeGa) is a promising candidate material due to its large magnetostriction (200 με), large piezomagnetic coefficient (5 ppm/Oe), and high stiffness (60 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, with a ferromagnetic resonance (FMR) linewidth of 10 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, resulting in a composite material with a small coercive field, narrow FMR linewidth, and high permeability (Rementer et al., 2017). Optical magnetostriction measurements confirmed that these laminates retain the large saturation magnetostriction of FeGa (200 με) while enhancing the piezomagnetic coefficient (7 ppm/Oe), allowing for optimal piezomagnetic actuation at substantially reduced magnetic bias fields. Furthermore, multiferroic composites incorporating these magnetic laminates were studied via polarized neutron reflectometry, demonstrating uniform rotation of the individual layers' magnetization with an applied electric field across distances much larger than the exchange length of either material.

Due to the metallic nature of these FeGa/NiFe multilayer composites, however, resulting devices would be inefficient due to the generation of eddy currents at high frequency. To mitigate these losses, ultrathin layers of Al_2O_3 were incorporated into the multilayer materials to reduce the conductivity and mitigate the generation of eddy currents. The effect of Al_2O_3 thickness, FeGa:NiFe volume ratio, and multilayer architecture on the soft magnetic properties was also studied, resulting in a 50% reduction in the FMR linewidth. Optimized magnetic laminates were shown to exhibit a small coercive field (<20 Oe), narrow ferromagnetic resonance linewidth (<50 Oe), and high relative permeability (>500) while maintaining excellent magnetoelastic coupling, showing great promise for the use of FeGa/NiFe/Al_2O_3 laminates in strain-mediated micro-scale communications systems.

9:20am **TF+EM+MI+MN+OX+PS-MoM4 Multiferroic Gd-substituted HfO_2Thin Films**, ***John Hayden**, F. Scurti, J. Schwartz, J.-P. Maria,* Pennsylvania State University

Modern ferroelectric technologies utilize perovskite structured materials, which have limited Si compatibility and modest bandgaps requiring thick films to reduce leakage current, hindering their implementation in realizable thin film devices. HfO_2 has been extensively researched as a gate dielectric thin film with excellent Si processing compatibility and has recently been found to exhibit ferroelectricity induced by a combination of impurity substitution, mechanical confinement by capping, intergranular surface area, and film thickness effects. This work investigates the microstructural characteristics, the ferroelectric response, and the potential for concomitant magnetic properties in sputtered Gd:HfO_2 thin films.

Gd-substituted HfO_2 thin films are a promising candidate as a multiferroic material, due to the presence of the magnetically active Gd^{3+} ion. Though substituting with Gd is known to induce ferroelectricity in HfO_2, the magnetic properties of Gd:HfO_2 have yet to be studied in depth. In this study, Gd:HfO_2 films are fabricated on TaN substrates by radio frequency sputtering of a composite Gd metal and HfO_2 oxide target in a mixed Ar and O_2 atmosphere. Grazing incidence x-ray diffraction is used to evaluate the suppression of the paraelectric monoclinic phase and stabilization of the ferroelectric orthorhombic phase. Electrical polarization measurements are used to study the room temperature spontaneous polarization in TaN/Gd:HfO_2/TaN metal-insulator-metal capacitors. Surface morphology of the films is characterized using atomic force microscopy, while magnetic properties are measured by variable temperature magnetometry. Initial magnetometry shows that Gd-substituted HfO_2 exhibits remnant magnetization at room temperature.

The scalability and simplicity of Gd:HfO_2, if it exhibits magnetoelectric coupling, make it an attractive model system for future developments in thin film multiferroics, having potential impacts for spintronics and other magnetoelectronic devices.

9:40am **TF+EM+MI+MN+OX+PS-MoM5 Epitaxial Growth of Antiferromagnetic NiO Films by Off-axis Sputtering for Spintronic Devices**, *A. Churikova, G.S.D. Beach,* Massachusetts Institute of Technology*; **Larry Scipioni**, A. Shepard, J. Greer, T. Newhouse-Illige,* PVD Products, Inc.

High-quality epitaxial growth of antiferromagnetic thin films is essential for future spintronic devices, as it allows small antiferromagnetic domain sizes and efficient electrical manipulation of domain walls via reading and writing currents. Antiferromagnetic materials are candidates for ultrafast operation due to THz antiferromagnetic spin dynamics, high packing densities due to the absence of stray magnetic fields, and stability due to insensitivity to external magnetic fields [1,2]. Meanwhile, the long spin diffusion lengths [3] and theoretically predicted superfluid transport of spin currents [4] in antiferromagnetic insulators are crucial for low-power device operation. The electrical control of magnetic spin textures has been thus far realized in epitaxially grown NiO on MgO substrates [5] and ferrimagnetic maghemite (γ−Fe2O3) and magnetite (Fe3O4) thin films [6].

We report the preparation of antiferromagnetic NiO thin films with (111) orientation on *c*-plane sapphire (1000) substrates by off-axis RF magnetron sputtering from a NiO target. The off-axis angle was 45°, and the sputtering pressure was 5 mTorr. Samples were grown with thicknesses ranging from 5 – 50 nm, and with growth temperatures from room temperature to 600°C, to determine optimum conditions. Structural characterization by x-ray diffraction demonstrates a high degree of epitaxy across a range of deposition temperatures and thicknesses. The deposition temperature and thickness dependence of epitaxial quality is investigated, with a characterization of the strain state, mosaicity, and crystallographic relationship between substrate and film. Evidence for antiferromagnetic order forming domains in NiO is provided via magnetic characterization of the films. Our results are essential for the optimization of the fabrication of high quality epitaxial antiferromagnetic films for practical spintronics devices.

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10:00am **TF+EM+MI+MN+OX+PS-MoM6 Structural and Magnetic Properties of CoPd Alloys for Non-Volatile Memory Applications**, *S. Gupta, J.B. Abugri, B.D. Clark,* University of Alabama*; P. Komninou,* Aristotle University of Thessaloniki*; **Sujan Budhathoki**, A.J. Hauser, P.B. Visscher,* University of Alabama

A study of perpendicular magnetic anisotropy (PMA) CoPd alloys is presented as a simple means of pinning MgO-based perpendicular magnetic tunnel junctions (pMTJs) for spin transfer torque magnetic tunnel junction (STT-MRAM) applications. A compositional study of the Co_xPd_{100-x} alloys at 50 nm thickness showed that the maximum coercivity and anisotropy was found for $Co_{25}Pd_{75}$. Perpendicular magnetic tunnel junction stacks were deposited using different compositions of CoPd. Current-in-plane tunneling measurements indicated that the TMR values roughly correlated with the coercivity and anisotropy of the single layers. A thickness study indicated that the alloy was fully perpendicular for thicknesses as low as 20 nm. Various seed layers were employed to optimize the coercivity of the $Co_{25}Pd_{75}$ layer. Magnetometry, X-ray diffraction (XRD), scanning electron microscopy (SEM) and high resolution transmission electron microscopy studies were carried out to relate the magnetic and structural properties of these layers. These studies showed that the highest coercivity $Co_{25}Pd_{75}$ was achieved on a seed layer of Ta/Pd which helped to crystallize the CoPd layer in an fcc (111) orientation.

10:40am **TF+EM+MI+MN+OX+PS-MoM8 Size Effects of the Electromechanical Response in Ferroic Thin Films: Phase Transitions to the Rescue**, ***Nazanin Bassiri-Gharb***, Georgia Institute of Technology **INVITED**

Silicon-integrated ferroelectric thin films have been leveraged over the last two decades for fabrication of high performance piezoelectric microelectromechanical systems (MEMS) devices. Ceramic $Pb(Zr_xTi_{1-x})O_3$(PZT) thin films have been often the material of choice, due to their large electromechanical response, especially at morphotropic phase boundary compositions (MPB at x ~0.52), where co-existence of multiple crystallographic distortions can enhance extrinsic electromechanical contributions. However, ferroelectric thin films suffer from extrinsic size effects that lead to deteriorated piezoelectric properties in thin and ultra-thin films. Here we report on different strategies for processing of thin films with enhanced piezoelectric response with respect to traditionally processed PZT thin films.

Specifically, we will discuss preparation of superlattice-like polycrystalline PZT thin films through chemical solution depositions, polycrystalline relaxor-ferroelectric thin films (PMN-PT), and finally alternative non-ferroelectric compositions, where the electric field-induced phase transitions can result in substantial enhancement in thinner films, even where traditional

11:20am **TF+EM+MI+MN+OX+PS-MoM10 Ferroelectrics Meet Ionics in the Land of van der Waals**, *S. Neumayer,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; J. Brehm,* Vanderbilt University*; M.A. McGuire,* Oak Ridge National Laboratory*; M.A. Susner,* Air Force Research Laboratory*; E. Eliseev,* National Academy of Sciences of Ukraine*; S. Jesse, S.V. Kalinin,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; A.N. Morozovska,* National Academy of Sciences of Ukraine*; S. Pantelides,* Vanderbilt University*; N. Balke, **Petro Maksymovych**,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Van der Waals crystals of metal thiophosphates can be thought of as derivatives of transition metal dichalcogenides where 1/3 of metal atoms is replaced with diphosphorous, thereby stabilizing the remaining 2/3 of metal ions in low oxidation states.1 Consequently, thiophosphates enable ultrathin magnetic, ferroelectric and Mott insulating materials, in q2D materials while also providing new opportunities for multifunctional interfaces .

Of particular interest is $CuInP_2S_6$, where ferroelectricity emerges out of ionically conducting state .2,3 In this work, we discuss unusual and perhaps anomalous properties observed in $CuInP_2S_6$ in both states.

$CuInP_2S_6$ exhibits giant negative electrostriction (Q_{33} = -3.2 m^4/C^2), which leads to large piezoelectric coefficients despite small polarization values and increase of Tc with applied pressure. It's the only material other than polymer PVDF for which such behavior is experimentally confirmed. Density functional theory reveals that the reason for negative electrostriction is a slight movement of Cu ions into the van der Waals gap due to anharmonicity of the potential well.4 Moreover, under high compressive strain, Cu starts to form interlayer bonds with sulfur across the van der Waals gap, leading to an additional phase of high polarization. Consequently, the potential distribution exhibits 4 instead of the usual two minima - a quadruple well, that is precisely tunable by strain. In the paraelectric state above ~70°C, Cu ion mobility drastically increases. Intriguingly, Cu can be reversibly extracted out of the lattice without visible damage. Finally, the selenide sibling $CuInP_2Se_6$, exhibits a lower transition temperature and propensity toward antiferroelectric ordering under the effect of depolarizing fields. In this material, we have for the first time observed piezoelectric response confined to domain walls (opposite to ferroelectrics), fulfilling the long-standing predictions for polar antiferroelectric domain walls and providing a new model system for emergent properties of topological defects in ferroic order parameter fields.

Research sponsored by Division of Materials Science and Engineering, Basic Energy Sciences, US Department of Energy. Microscopy was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

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11:40am **TF+EM+MI+MN+OX+PS-MoM11 Adsorption-controlled Epitaxial Growth of the Hyperferroelectric Candidate LiZnSb on GaSb (111)**, *D. Du, P. Strohbeen,* University of Wisconsin - Madison*; H. Paik,* Cornell University*; C. Zhang, P. Voyles,* ***Jason Kawasaki,*** University of Wisconsin - Madison

A major challenge for ferroelectric devices is the depolarizing field, which competes with and often destroys long-range polar order in the limit of ultrathin films. Recent theoretical predictions suggest a new class of materials, termed hyperferroelectics [1], should be immune to the depolarizing field and enable ferroelectric devices down to the monolayer limit. Here we demonstrate the epitaxial growth of hexagonal LiZnSb, one of the hyperferroelectric candidate materials, on GaSb (111) substrates. Due to the high volatility of all three atomic species, we find that stoichiometric films can be grown in a thermodynamically adsorption-controlled window, using an excess zinc flux. Outstanding challenges remain in controlling the point defects of LiZnSb and in controlling polytypism. While the films primarily grow in a hexagonal "stuffed wurtzite" phase (space group $P6_3mc$), which is has the desired polar structure, there exists a competing cubic "stuffed zincblende" polymorph that is nonopolar (*F-43m*). We will discuss our strategy towards controlling defects and polytypism in LiZnSb, which is based in large part on the wurtzite – zincblende polytypism observed in InAs. We will also present preliminary electrical measurements on phase pure ferroelectric capacitor structures.

This work was supported by the Army Research office (W911NF-17-1-0254) and the National Science Foundation (DMR-1752797).

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2D Materials
Room A226 - Session 2D+AP+EM+MI+MN+NS+PS+TF-MoA
Nanostructures including Heterostructures and Patterning of 2D Materials

Moderator: Deep Jariwala, University of Pennsylvania

1:40pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA1 Tailoring and Patterning 2D Material Interfaces Through Chemical Functionalization*, Arend van der Zande,*** University of Illinois at Urbana-Champaign **INVITED**

Two-dimensional materials are all surface, so any change in the surface chemistry affects the entire material. This offers a challenge and an opportunity to engineering the material properties and new device behavior. There are many strategies to altering the chemical structure of 2D materials, yet one of the most successful is the chemical functionalization with low energy plasmas such as hydrogen and fluorine. Functionalization enables phase changes within materials to dramatically alter their properties, can be applied post synthesis and device fabrication, and is compatible with lithography for spatial patterning. Most studies of chemical functionalization focus on single functionalization of single 2D materials, yet there are many opportunities when applying the principles of chemical functionalization to spatially engineer the properties though in plane interfaces or out of plane in heterostructures.

First, we will examine selective etching with XeF_2 to pattern heterostructures using graphene etch stops. These techniques are self-limiting, yet scalable, and enable the patterning of 2D heterostructures into 3D multilayer circuitry. Moreover, devices like encapsulated graphene transistors fabricated with these techniques have exceptionally low contact resistances and mobilities which approach theoretical limits.

Second we will present a new strategy for tailoring the stoichiometry of functionalized graphene compounds through the systematic control of the ratio between adatoms. We demonstrate new ternary HFG compounds and reversible switching of material stoichiometry via the sequential exposure of graphene to low energy H plasma and XeF_2 gas. By patterning regions of different functionalization on a single chip, we perform direct comparisons and show spatially controlled tuning of the relative surface properties such as wettability, friction, electronic conductivity and molecular adhesion. Taken together, these studies show that chemical functionalization offers new atomically precise nanofabrication and materials engineering techniques for scalable engineering of circuitry along all three dimensions.

2:20pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA3 Dual-Route Hydrogenation of the Graphene/Ni Interface*, Rosanna Larciprete,*** CNR-Institute for Complex Systems, Roma, Italy*; D. Lizzit,* Elettra - Sincrotrone Trieste, Trieste, Italy*; M.I. Trioni,* CNR-Institute of Molecular Science and Technologies, Milano, Italy*; P. Lacovig, L. Bignardi, S. Lizzit,* Elettra - Sincrotrone Trieste, Trieste, Italy*; R. Martinazzo,* Università degli Studi di Milano, Milano, Italy

Although the high surface-to-weight ratio would make graphene (Gr) one of the most promising material for hydrogen accumulation, up to now only moderate gravimetric density values of 1-2% have been obtained at room temperature (RT). The ultimate H coverage is limited by the competition between the adsorption and desorption/abstraction processes and by the elastic energy that accumulates in the C lattice once puckered by the local sp3rehybridization of the C atoms binding hydrogen. Moreover, for epitaxial Gr on metals, the substrate-induced Gr corrugation might modulates periodically H adsorption. In this respect, the Gr/Ni(111) interface appears much more favorable than other graphene/metal systems, as the limitations due to the presence of the moirè supercell vanish due to commensurate relation between the Gr and Ni(111) lattices. Moreover, hydrogenation might be favored by the peculiar reactivity of Gr/Ni(111).This issues motivated a re-investigation of the interaction of this particular interface with hydrogen.

In this study [1]we used x-ray photoelectron spectroscopy (XPS) and near edge x-ray absorption fine structure spectroscopy (NEXAFS) to follow the RT hydrogenation of Gr/Ni(111) and determined the configuration of the hydrogenated interface by scanning tunneling microscopy (STM). We found that hydrogenation proceeds through a dual path that includes hydrogen chemisorption on top of the graphene followed by a slow but continuous intercalation below graphene. At low coverage H atoms predominantly adsorb as monomers and chemisorption saturates when ≈ 25% of the surface is hydrogenated. The formation of C−H bonds determines new components in the C 1s core level spectrum that are attributed by DFT calculations to C atoms directly bonded to H and to their first neighbors. In parallel with chemisorption, with a much lower rate, H atoms intercalate below Gr and bind to Ni surface sites. Thermal programmed desorption measurements showed that chemisorbed hydrogen is released around 600 K, whereas the intercalated phase desorbs abruptly slightly below 400 K. Then the Gr cover, besides offering a storage volume for the intercalated H, stabilizes it above room temperature rising by a few tens of kelvins the H2 release temperature with respect to the bare Ni(111) surface.

The effectiveness of these results can be expanded by using Ni substrates with large specific surface, as nanoparticles or nanostructured foils, which, when covered with Gr, might become media where hydrogen can be loaded and stored above room temperature.

[1] D. Lizzit et al. ACS Nano 13 (2019) 1828

2:40pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA4 Assembly of Arrays of Predefined Monolayer Features into vdW Heterostructure by a Continuous Exfoliate-align-Release Process*, Vu Nguyen,*** *H. Taylor,* University of California at Berkeley

One of the major challenges of van der Waals (vdW) integration of 2D materials is the high-yield and -throughput assembly of pre-defined sequence of monolayers into heterostructure arrays. Although a variety of techniques have been developed to exfoliate the 2D materials from the source and deterministically place them onto a target substrate, they typically can transfer only either a wafer-scale blanket or a small flake at a time with uncontrolled size and shape. Here we present a method to exfoliate arrays of lithographically defined monolayer MoS_2 and WS_2 features from multilayer sources and directly transfer them in a deterministic manner onto target substrates. The continuous exfoliate-align-release process, without the need of an intermediate carrier substrate, was enabled by a new transfer medium fabricated by spin-coating a low-crosslinked and transparent adhesive on a transparent, electrostatically active backing material with low surface energy. MoS_2/WS_2 vdW heterostructure arrays produced by this method were characterized, showing coupled photoluminescence between the monolayers. Light-emitting devices using WS_2 monolayer were also demonstrated, proving the functionality of the fabricated materials. This method promises to produce large-area monolayer and multiplex heterostructure arrays with capability to integrate with existing semiconductor manufacturing equipment.

3:00pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA5 van der Waals Heterojunction Photothermoelectric Effect in MoS_2/Graphene Monolayers*, Yunqiu Kelly Luo,*** The Ohio State University*; T. Zhou,* University at Buffalo, State University of New York*; M. Newburger,* The Ohio State Univesity*; R. Bailey-Crandell, I. Lyalin,* The Ohio State University*; M. Neupane,* U.S. Army Research Laboratory*; A. Matos-Abiague,* Wayne State University*; I. Zutic,* University at Buffalo, State University of New York*; R. Kawakami,* The Ohio State University

Two-dimensional (2D) van der Waals (vdW) heterostructures provide a vast playground for exploring new phenomena due to its unique ability to tailor and combine dissimilar materials with atomic precision. In particular, the combination of graphene and transition metal dichalcogenides (TMDC) garners immense interest due to their novel optoelectronic, valleytronic and spintronic properties. Here, we report the observation of a highly tunable vdW heterojunction photothermoelectric effect (HPTE) in dual-gated MoS_2/graphene heterostructures, identified by a signature six-fold photocurrent pattern as a function of heterojunction bias and carrier density. In stark contrast to photovoltaic and photothermionic effects, we discover a new mechanism arising from photoexcitation of hot electrons in graphene and subsequent thermoelectric transport across the vdW junction. While analogous to lateral photothermoelectric effects at quasi-1D junctions in single layers, the vertical geometry of HPTE offers area scaling of 2D active regions and establishes, for the first time, the photothermoelectric response in vdW heterostructures. Operating at both low (18 K) and room temperatures, the discovery of HPTE creates new

possibilities for electrically-tunable broadband photodetectors and atomically-thin spin caloritronic devices.

3:20pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA6 Formation of Edge-bonded MoS_2-graphene Nanoribbons by On-surface Synthesis**, ***Mark Haastrup****, M. Mammen, J. Rodríguez-Fernández, J.V. Lauritsen,* Aarhus University, Denmark

2D materials exhibiting unique material properties have the potential for a huge impact on our future. Graphene, as the first discovered truly 2D material, has been extensively studied. However, the lack of an intrinsic band gap makes it inadequate for electronic and optical devices. MoS_2 from the family of transition metal dichalcogenides has been intensively investigated for its possibility to be used in future applications. The vision is to integrate various 2D materials to realise an actual device. However, the actual assembly of these materials with high controllability remains a challenge. Vertical heterostructures, supported by Van der Waals interactions, have already been realised by manually stacking 2D materials on top of each other[1]. An ultimate thin device can be realised by creating lateral heterostructures with atomically sharp interfaces where each material is directly bonded to another. Currently, methods for in-plane bonding of MoS_2 to other materials (e.g. graphene) are limited due to poor structural match. One possible solution is to develop selective bottom-up methods for synthesis of molecular nanostructures by self-assembly.

This study aim to investigate the fundamental nature of bonding of graphene nanoribbons (GNRs) to the edges of MoS_2 nanoparticles by scanning tunnelling microscopy (STM). The aim is to synthesise GNRs from precursor molecules through a thermally activated Ullmann reaction already used elsewhere[2,3]. After initial growth of MoS_2, it is necessary to anneal in a hydrogen atmosphere to activate the edges to facilitate the attachment of an intermediate structure of poly(para-phenylene) (PPP) wires. STM reveals the PPP wires have an affinity for the corners of the MoS_2 nanoparticles with a distance, obtained from line scans across the adsorption site, consistent with a covalent C-S bond.

[1]: Pant et al., Nanoscale, 2016, 8, 7, 3870-3887

[2]: Cai et al., Nature, 2010, 466, 7305, 470–473

[3]: Basagni et al., J. Am. Chem. Soc., 2015, 137, 5, 1802-1808

4:00pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA8 The Effects of Metal-modification and Two Dimensional (2D) Lamellar Structure on Catalytic Performance of MFI Zeolite for Ethylene Conversion into Liquid Aromatics**, ***Laleh Emdadi****, L. Mahoney, D. Tran, I. Lee,* US Army Research Laboratory

The effects of two dimensional (2D) meso-/microporous structure and metal modification with gallium or zinc on catalytic performances of lamellar MFI zeolites in ethylene conversion reaction to liquid aromatics were investigated. Dual template technique was used to synthesize the 2D zeolite and metal modification of the zeolite was carried out by wet impregnation method. The results of multiple analysis techniques such as TEM, XRD, Ar adsorption-desorption, UV-Visible spectroscopy, and H_2-TPR showed that the zeolite structure is a pivotal factor for controlling the type of metal dopant species forming on zeolite, their size, and their distribution. Adding metal dopants to 2D zeolite structures improved the yield of liquid aromatics and selectivity for mono-benzene alkylated aromatics compared to their microporous commercial MFI analogies while decreased the coke formation rate. Zinc loaded lamellar MFI had the most efficient catalytic performance among all studied catalysts with lowest amount of total coke and highest fraction of light coke including mono-benzene alkylated aromatics determined by combination of different techniques such as FTIR, UV-Vis, MS-temperature programmed oxidation (TPO), FTIR-TPO, and GC-MS. This can be explained by higher accessibility of reactants to active sites and facilitated transport of products and coke precursors from lamellar structure of this zeolite and the lower Brønsted/Lewis acid site ratio of this catalyst provided by metal modification which is more suitable for ethylene aromatization and suppresses the formation of heavy coke species. The catalytic performance of zeolite catalyst can be tuned by modulating both the textural and acidity properties of the zeolite structure. The metal modified 2D lamellar MFI zeolites as bifunctional catalysts open an avenue for converting large reactant molecules to desired products by designing a catalyst with an optimal structure, acidity, and dispersion of metal dopants.

4:20pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA9 Structural Stability of Graphene Nanoflakes:From the View Point of Aromaticity**, *M. Ushirozako, H. Matsuyama, A. Akaishi,* ***Jun Nakamura****,* The University of Electro-Communications (UEC-Tokyo), Japan

Recently, nano-scale graphene nanoflakes (GNFs) have attracted great attention as one of the promising materials for electronics and spintronics. Kim *et al*. have successfully fabricated GNFs with various sizes up to 35 nm and have reported that the photoluminescence property of GNFs depends on the size and the edge shape [1]. From the view point of the structural stability of GNFs, we have not yet acquired the systematic comprehension with regard to effects of shapes and sizes of GNFs on the stability. In the present study, we have examined how the stability of GNFs is dominated by the edge shape and the size of GNFs, using first-principles calculations within the density functional theory.

In order to evaluate the stability of GNFs, we calculated the edge formation energy. First, we consider GNFs with the six-fold symmetry (D_{6h}) and classify them into zigzag GNFs (ZZGNFs) and armchair GNFs (ACGNFs). ACGNFs have two subtypes, AC(1) and AC(2), depending on whether carbon atoms are just at the corner of the outermost envelope hexagon of GNFs. We define the edge purity as the ratio of the number of carbon atoms at the edge unambiguously regarded as the armchair to the total number of edge atoms. The purity of AC(1) is higher than that of AC(2). The chemical formulae associated with ZZ, AC(1), and AC(2) are $C_{6n^2}H_{6n}$, $C_{18n^2-18n+6}H_{12n-6}$, $C_{18n^2-30n+12}H_{12n-12}$, respectively. In addition, we also evaluate the structural stabilities of triangular and rhombus GNFs.

We calculated the edge formation energy of the GNFs having up to 1200 carbon atoms as a function of the number of edge carbon atoms [3]. The formation energy of ZZGNFs is higher than that of ACGNFs irrespective of the size of GNFs. This instability of ZZGNFs is attributed to the presence of the so-called edge state. Indeed, it has also been shown that the formation energy of the zigzag graphene nanoribbon is higher than that of the armchair one [4]. It is noted that AC(2) is slightly more stable than AC(1), whereas the purity of AC(2) is lower than that of AC(1). Such peculiar stabilization can be reasonably explained in terms of the aromaticity of GNFs. The Nucleus Independent Chemical Shifts (NICS) values, which is averaged for the six-membered rings in GNFs, for AC(2) are lower than those for AC(1). This means AC(2) is more aromatic than AC(1). We will discuss the quantitative relationship between the stability and the aromaticity of GNFS.

[1] S. Kim et al., ACS Nano, **6**, 9, 8203 (2012)

[2] W. Hu *et al*., J. Chem. Phys. **141**, 214704 (2014)

[3] A. Akaishi, M. Ushirozako, H.Matsuyama, andJ.Nakamura, Jpn.J.Appl.Phys. **57**, 0102BA(2018)

[4] S. Okada. Phys. Rev. B, **77**, 041408 (2008)

4:40pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA10 Wafer-scale 2D-3D Mixed Heterostructures Enabled by Remote Epitaxy through Graphene**, ***Jeehwan Kim****,* Massachusetts Institute of Technology **INVITED**

The current electronics industry has been completely dominated by Si-based devices due to its exceptionally low materials cost. However, demand for non-Si electronics is becoming substantially high because current/next generation electronics requires novel functionalities that can never be achieved by Si-based materials. Unfortunately, the extremely high cost of non-Si semiconductor materials prohibits the progress in this field. Recently our team has invented a new crystalline growth concept, termed as "remote epitaxy", which can copy/paste crystalline information of the wafer remotely through graphene, thus generating single-crystalline films on graphene [1,2]. These single-crystalline films are easily released from the slippery graphene surface and the graphene-coated substrates can be infinitely reused to generate single-crystalline films. Thus, the remote epitaxy technique can cost-efficiently produce freestanding single-crystalline films including III-V, III-N, and complex oxides. This allows unprecedented functionality of flexible device functionality required for current ubiquitous electronics. I will also present detailed mechanism behind remote atomic interaction through graphene [2]. In addition, we have recently demonstrated a manufacturing method to manipulate wafer-scale 2D materials with atomic precision to form monolayer-by-monolayer stacks of wafer-scale 2D material heterostructures [3]. In this talk, I will discuss the implication of this new technology for revolutionary design of next generation electronic/photonic devices with combination of 3D/2D mixed heterostructures.

[1] Y. Kim, et al, and J. Kim, "Remote epitaxy through graphene enables two-dimensional material based layer transfer" ***Nature***, Vol. 544, 340 (2017)

[2] W. Kong, et al, and J. Kim, "Polarity govern atomic interaction through two-dimensional materials", ***Nature Materials***, Vol. 17, 999 (2018)

[3] J. Shim, S. Bae, et al, and J. Kim, "Controlled crack propagation for atomic precision handling of wafer-scale two-dimensional materials" ***Science***, 362, 665 (2018)

2D Materials
Room A216 - Session 2D+AP+EM+MI+NS+PS+TF-MoA
2D Materials Growth and Fabrication

Moderator: Sarah Haigh, University of Manchester, UK

2:00pm **2D+AP+EM+MI+NS+PS+TF-MoA2 Synthesis of High Quality Monolayer Transition Metal Dichalcogenides using Direct Liquid Injection***,* ***Kathleen M. McCreary****, E.D. Cobas, A.T. Hanbicki, M.R. Rosenberger, H.-J. Chuang, B.T. Jonker,* U.S. Naval Research Laboratory

In recent years, interest in monolayer transition metal dichalcogenides (TMDs) has rapidly increased, spurred by the possibility for integration into a variety of technologies such as photodetection, flexible electronics, and chemical sensing. While fundamental investigations can be performed on exfoliated flakes or chemical vapor deposition synthesized isolated islands, the limited size resulting from these techniques poses a significant barrier forimplementation of TMDs in technological applications. To overcome these obstacles, new synthesis avenues should be explored. Here, we outline a novel technique that utilizes a commercially available Anneal Sys growth chamber equipped with direct liquid injection (DLI) heads for all precursors. The use of liquid, rather than solid precursors, provides fine control of both metal and chalcogen precursors leading to the synthesis of monolayer MoS_2 across cm^2 areas. Photoluminescence, Raman, XPS, and conductive AFM are used to evaluate DLI grown MoS_2, and indicate high quality material having low defect density, with metrics comparable to or better than exfoliated and chemical vapor deposition grown MoS_2.

2:20pm **2D+AP+EM+MI+NS+PS+TF-MoA3 Understanding and Controlling the Growth of 2D Materials with Non-Equilibrium Methods and in situ Diagnostics***,* ***David Geohegan****, Y-C. Lin, Y. Yu,* Oak Ridge National Laboratory*; C. Liu, G. Duscher,* University of Tennessee Knoxville*; A. Strasser,* University of Texas at Dallas*; A.A. Puretzky,* Oak Ridge National Laboratory*; K. Wang,* Intel Corporation, USA*; M. Yoon, C.M. Rouleau,* Oak Ridge National Laboratory*; S. Canulescu,* DTU Nanolab, Technical University of Denmark*; P.D. Rack,* University of Tennessee Knoxville*; L. Liang, W. Zhang, H. Cai, Y. Gu, G. Eres, K. Xiao,* Oak Ridge National Laboratory **INVITED**

Atomically-thin two-dimensional (2D) materials, including layered 2D transition metal dichalcogenide (TMD) semiconductors and their heterostructures, exhibit remarkable quantum properties that are envisioned for energy-efficient photovoltaics, flexible optoelectronics, catalysis, and quantum information science. However, significant synthesis and processing challenges currently limit the technologic development of these "all-surface" materials, including wafer-scale, bottom-up synthesis of uniform layers of crystalline 2D materials that are comparable in quality to exfoliated flakes of bulk materials. As-synthesized crystals of 2D TMDs display remarkable heterogeneity on both the atomistic level (e.g., vacancies, dopants, and edge terminations) and on the mesoscopic length scale (e.g., misoriented grains, layer orientations, and interactions with substrates and adsorbates) that can strongly influence the structure and electronic properties in 2D materials. This heterogeneity offers a serious challenge for synthesis and processing, yet offers a tremendous opportunity to tailor functionality.

Here we describe several approaches that are being developed for in situ diagnostic analysis and control of synthesis and heterogeneity. In addition to conventional vapor transport techniques, progress in laser-based approaches for 2D synthesis and modification, such as pulsed laser deposition (PLD) and pulsed laser conversion of precursors, are presented that permit control of the growth environment using time-resolved in situ diagnostics. The non-equilibrium advantages of PLD to form alloys and vertical heterojunctions are demonstrated using the tunable kinetic energy and digital nature of the process. Correlated atomic-resolution electron microscopy and atomistic theory are used to understand the size and stoichiometry of the "building blocks" deposited for synthesis and the forces that guide assembly. 2D crystals are grown directly on TEM grids within custom chambers and transmission electron microscopes where the ability to 'see' every atom in these atomically-thin crystals permits a unique opportunity to understand the forces governing their synthesis and functionality. In situ optical spectroscopy techniques are described to characterize the material's evolving structure and properties, offering the opportunity to 'close the loop' between synthesis and optoelectronic functionality of 2D materials and heterostructures.

Research sponsored by the U.S. Dept. of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Div. (synthesis science) and Scientific User Facilities Div. (characterization science).

3:00pm **2D+AP+EM+MI+NS+PS+TF-MoA5 Area-Selective Atomic Layer Deposition of 2D WS_2 Nanolayers***,* ***Shashank Balasubramanyam*** [1]*,* Eindhoven University of Technology, The Netherlands, Noord Brabant*; M.J.M. Merkx,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; A.J.M. Mackus,* Eindhoven University of Technology, The Netherlands, Nederland*; A.A. Bol,* Eindhoven University of Technology, The Netherlands, Netherlands

With continued downscaling of device dimensions, ultra-thin two dimensional (2D) semiconductors like WS_2 are considered as promising materials for future applications in nanoelectronics. At these nanoscale regimes, device fabrication with precise patterning of critical features is challenging using current top-down processing techniques. In this regard, area-selective atomic layer deposition (AS-ALD) has emerged as a promising candidate for bottom-up processing to address the complexities of nanopatterning. Till date, AS-ALD of metals[1] and dielectrics[2] have been successfully demonstrated. However, AS-ALD of 2D materials has remained elusive. In this contribution, we demonstrate area-selective deposition of 2D WS_2 nanolayers by using a three-step (ABC-type) plasma-enhanced ALD process.

AS-ALD of WS_2 was achieved by using acetylacetone (Hacac) inhibitor (A), bis(tertbutylimido)-bis(dimethylamido)-tungsten precursor (B), and H_2S plasma (C) pulses. This process resulted in immediate growth on SiO_2 while a significant nucleation delay was observed on Al_2O_3, as determined from *in-situ* spectroscopic ellipsometry (SE) and *ex-situ* X-ray photoelectron spectroscopy (XPS) measurements. The surface chemistry of this selective process was analysed by *in-situ* Fourier transform infrared spectroscopy (FTIR). The analyses revealed that the inhibitor adsorbed on the Al_2O_3 surface, blocking precursor adsorption, while little or no inhibitor adsorption was detected on the SiO_2 surface where WS_2 was readily deposited. Furthermore, the area-selective growth was demonstrated on SiO_2 samples with patterned Al_2O_3 on top. On SiO_2, WS_2 could be deposited with angstrom-level thickness control.

To improve the crystallinity, the AS-ALD WS_2 films were annealed at temperatures within the thermal budget of industrial semiconductor processing (≤ 450°C). The annealed films exhibited sharp Raman peaks, which is a fingerprint of highly crystalline WS_2. Furthermore, Raman line scans over the patterns showed very sharp peak intensity transitions at the SiO_2-Al_2O_3 interface which confirmed that annealing had no impact on selectivity.

To summarize, this work pioneered the combination of two key avenues in atomic-scale processing: area-selective growth and ALD of 2D materials. It is expected that the results of this work will lay the foundation for area-selective ALD of other 2D materials.

[1] R. Chen and S.F. Bent, *Adv. Mater.* (2006).

[2] A. Mameli, M.J.M. Merkx, B. Karasulu, F. Roozeboom, W.M.M. Kessels and A.J.M. Mackus, *ACS Nano* (2017).

3:20pm **2D+AP+EM+MI+NS+PS+TF-MoA6 Growth Behavior of Hexagonal Boron Nitride on Cu-Ni Binary Alloys***,* ***Karthik Sridhara,*** Texas A&M University*; J.A. Wollmershauser,* U.S. Naval Research Laboratory*; L.O. Nyakiti,* Texas A&M University*; B.N. Feigelson,* U.S. Naval Research Laboratory

Controlled growth of large area n-layered chemical vapor deposited (CVD) hexagonal boron nitride (h-BN) is of great interest as a tunnel dielectric, and substrate for graphene and transition metal dichalcogenides (TMDs). The CVD growth of h-BN has been demonstrated on various transition metal catalytic substrates such as Cu, Ni, Pt and Fe. Of these metal substrates, Cu and Ni are frequently used due to their relative abundance and low cost. However, h-BN growth on Cu leads to monolayer films, and growth on Ni yields thicker, substrate grain-dependent films. Therefore, a

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

cost-effective transition metal substrate is needed that will facilitate controlled n-layered h-BN growth.

In this work, we prepare isomorphous Cu-Ni binary alloys from 10-90 wt.% Ni by creating Ni-rich (Ni-Cu) and Cu-rich (Cu-Ni) alloys using electroplating of Cu on Ni foils and Ni on Cu foils, respectively. The electroplated foils are then annealed at ~1030° C for >5 hours to create Ni-Cu and Cu-Ni alloys. The alloys are subsequently polished mechanically to create a planarized surface suitable for h-BN growth. The surface morphology before and after polishing is assessed using a scanning electron microscope (SEM). Energy dispersive spectroscopy (EDS) characterization of the alloys confirms a designed stoichiometry at every weight percent. h-BN is grown on the alloys using atmospheric pressure chemical vapor deposition (APCVD) at 1030° C, with ammonia borane as the precursor, and H_2/N_2 as the carrier gas flowing at ~200 sccm. Cu and Ni foils are used as control samples for this study. Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS) is used to confirm and characterize h-BN growth directly on Cu, Ni and alloy substrates. SEM is performed to evaluate the h-BN film and crystal morphology. The results indicate that the h-BN growth behavior on Ni-Cu is different than on Cu-Ni alloys. A trend of decreasing h-BN amount with reducing Ni concentration is observed on Ni-Cu alloys while no such trend is observed on Cu-Ni alloys. Additionally, there are large (~20 µm) multilayer and monolayer single crystals of h-BN on Ni-Cu alloys, and predominantly monolayer crystals and films of h-BN on Cu-Ni alloys. The difference in growth behavior is studied using x-ray photoelectron spectroscopy (XPS) and electron backscattering diffraction (EBSD), which reveal that the alloy surface composition determines the h-BN growth. This work demonstrates how Cu-Ni alloy substrate of different compositions, along with CVD growth conditions, can be used to control h-BN growth.

4:20pm **2D+AP+EM+MI+NS+PS+TF-MoA9 Controlled Growth of Transition Metal Dichalcogenide Monolayers for Applications in Nanoelectronic and Nanophotonic Devices***, A. George, C. Neumann, D. Kaiser, R. Mupparapu,* Friedrich Schiller University Jena, Germany*; U. Hübner,* Leibniz Institute of Photonic Technology, Jena, Germany*; Z. Tang, A. Winter, I. Staude,* ***Andrey Turchanin,*** Friedrich Schiller University Jena, Germany

Controlling the flow rate of precursors is highly essential for the growth of high quality monolayer crystals of transition metal dichalcogenides (TMDs) by chemical vapor deposition. Thus, introduction of an excess quantity of precursors affects the reproducibility of the growth process and results in the multilayer growth. Here, we demonstrate the use of Knudsen-type effusion cells for controlled delivery of sulfur precursor for the large area, high density, size-controlled and highly reproducible growth of monolayer TMD crystals [1]. The size of the grown crystals can be tuned between 10 - 200 µm. We grow MoS_2, WS_2, $MoSe_2$ and WSe_2 monolayer crystals as well as $MoSe_2$-WSe_2 lateral heterostructures and characterize them by optical microscopy, atomic force microscopy, Raman spectroscopy, photoluminescence spectroscopy and electrical transport measurements. It has been found that they possess a high crystalline, optical and electrical quality based on their single crystalline nature. We demonstrate their implementation in novel field-effect and nanophotonic devices and discusse an influence of the point defect density on their functional characteristics [2-3]. Moreover, we present a novel synthetic route for the integration of TMDs into lateral heterostructures with other 2D materials [4].

[1] A. George et al., *J. Phys.: Mater.* 2 (2019) 016001.

[2] T. Bucher et al., *ACS Photonics* 6 (2019) 1002.

[3] R. Meyer et al., *ACS Photonics* 6 (2019) DOI: 10.1021/acsphotonics.8b01716

[4] A. Winter et al., *Carbon* 128 (2018)106.

4:40pm **2D+AP+EM+MI+NS+PS+TF-MoA10 Atomic Layer Deposition of BN as a Novel Capping Barrier for B_2O_3*, Aparna Pilli,*** *J. Jones, J.A. Kelber,* University of North Texas*; A. LaVoie, F. Pasquale,* Lam Research Corporation

The deposition of boron oxide (B_2O_3) films on Si and SiO_2 substrates by atomic layer deposition (ALD) is of growing interest in microelectronics for shallow doping of high aspect ratio transistor structures. B_2O_3, however, forms volatile boric acid (H_3BO_3) upon ambient exposure, requiring a passivation barrier, for which BN was investigated as a possible candidate. Here, we demonstrate, deposition of BN by sequential BCl /NH reactions at 600 K on two different oxidized boron substrates: (a) B O deposited using BCl /H O ALD on Si at 300 K ("B O /Si"); and (b) a boron-silicon oxide formed by sequential BCl /O reactions at 650 K on SiO followed by annealing to 1000 K ("B-Si-oxide"). X-ray photoelectron spectroscopy (XPS) data demonstrate layer-by-layer growth of BN on B_2O_3/Si with an average growth rate of ~1.4 Å/cycle, accompanied by some B_2O_3 removal during the first BN cycle. In contrast, continuous BN growth was observed on B-Si-oxide without any reaction with the substrate. XPS data also indicate that the oxide/nitride heterostructures are stable upon annealing in ultrahigh vacuum to >1000 K. XPS data, after the exposure of these heterostructures to ambient, indicate a small amount of BN oxidation at the surface NH species, with no observable hydroxylation of the underlying oxide films. These results demonstrate that BN films, as thin as 13 Å, are potential candidates for passivating boron oxide films prepared for shallow doping applications.

5:00pm **2D+AP+EM+MI+NS+PS+TF-MoA11 Atomic Layer Deposition of SiO_2 on Group VIII Metals: Towards Formation of a 2D Dielectric***, T. Suh, R. Yalisove,* ***James Engstrom,*** Cornell University

The atomic layer deposition (ALD) of many metals, particularly Group VIII (now known as Groups 8, 9 and 10), on SiO_2 has been an active area of research in many fields, which include microelectronics and heterogeneous catalysis. There have been many fewer studies of the inverse—the deposition of SiO_2 on many of these same metals. One possible reason to explore the ALD growth of SiO_2 on transition metals is that it might provide a route to an atomically thick SiO_2 dielectric, *silicatene*. Silicatene is a 2D material that consists of a bilayer of Si_2O_3 linked to each other by bridging oxygen atoms (giving SiO_2), where there are no dangling bonds or covalent bonds to the underlying substrate on which it is grown. For example, an established route to form silicatene involves deposition of elemental Si in UHV and subsequent high-temperature annealing on various single-crystalline metal surfaces including, but not limited to, Ru(0001), Pt(111), and Pd(100). Such a process, unfortunately, is likely not compatible with high-volume manufacturing. With this motivation we embarked on a study of the plasma-assisted ALD of SiO_2 on e-beam deposited polycrystalline thin films of Ru, Pt and Pd using a commercial ALD reactor. We analyzed both the thin films and the starting substrates using a combination of techniques including contact angle, spectroscopic ellipsometry (SE) and X-ray photoelectron spectroscopy. Thin films of SiO_2 were deposited using tris(dimethylamido)silane and an oxygen plasma at a substrate temperature of 200 °C, and we examined growth for 5, 10, 20, 50 and 100 cycles. Contact angle measurements showed immediate evidence for SiO_2 deposition on all metal surfaces, and the contact angle decreased and remained constant and < 10° from 5 to 100 cycles of ALD. From SE we found little evidence of an incubation period, and growth was linear for the range of sample examined and the thickness deposited per cycle was remarkably constant at a value of 0.76-0.78 Å-cycle^{-1}. Analysis of these films using angle-resolved XPS was consistent with the formation of a thin film of SiO_2 with uniform thickness. Having characterized the thin film thickness-ALD cycle relationship we subjected SiO_2 thin films with thickness of ~ 7-15 Å to post-deposition high-temperature anneals in oxygen furnace. Initial attempts to form silicatene with an anneal at 800 °C, produced a structure suggesting possible interfacial reaction between the SiO_2 and Ru, perhaps involving silicide formation. We will end our presentation with a discussion of recent work involving a more extensive examination of the post-deposition annealing step, and deposition on patterned wafers.

Electronic Materials and Photonics Division
Room A214 - Session EM+PS+TF-MoA

New Devices and Materials for Logic and Memory

Moderator: Rehan Kapadia, University of Southern California

1:40pm **EM+PS+TF-MoA1 Short-term Plasticity to Long-term Plasticity Transition Mimicked by High Mobility InP FETs with TiO_2 Trapping Layer***, Jun Tao,*** *R. Kapadia,* University of Southern California

Memory is widely believed to be encoded and stored in the central nervous system by altering the synapse strength via activity-dependent synaptic plasticity between millions of neurons in vertebrates. Consolidations from short-term plasticity (STP) to long-term plasticity (LTP) not only transform the important external stimuli to permanently stored information but release storage space for accepting new coming signals. Although memristor technology (e.g. RRAM) has been reported to mimic the STP and LTP characteristics and exhibited its merit in density comparing to traditional CMOS based SRAM technology, some conventional memristors suffer non-ideal operation speed, small dynamic range, and high resistance variation.

In our work, the single crystal Indium Phosphide (InP) based synaptic devices demonstrated its advantages not only in the emulation of the synaptic functions for both STP and LTP characteristics but also in the controllability of transition from STP to LTP. Since we interpret gate voltage pulses as the pre-synaptic action potentials, the source-drain current as post-synaptic current, and the channel conductance as synaptic weight, the consolidations from STP to LTP are elaborately demonstrated through mediating multiple action potential parameters like pulse numbers, pulse intervals (or rates), and pulse durations. The synaptic devices we demonstrated here are essentially single crystal channel InP Field Effect Transistors (FETs) fabricated on Si/SiO_2 substrates with the templated liquid-phase (TLP) method. In addition, TiO_2 trapping layer is inserted into the gate dielectric layer to provide extra deeper trap states. The 'ratchet' mechanism is utilized to have the charges 'fall' into the TiO_2 well and implement the transition from STP to LTP effectively.

2:00pm **EM+PS+TF-MoA2 Magnetic Domain Wall Devices for Artificial Neural Network**, ***Saima Siddiqui**, S. Dutta, A. Tang, L. Liu, M. Baldo, C. Ross,* MIT

Magnetic domain wall devices are promising candidates for logic [1] and storage class memory [2]. Due to the non-volatility and energy-efficient switching, this type of device is one of the prime candidates for in memory computing and brain-inspired computing. In-memory computing is a non-von-Neumann architecture where data computation and storage are done locally to reduce the data movement between the processor and the storage memory [3]. The layer-by-layer operations of data require synapses (i.e. variable resistors whose resistance vary linearly with the input) and activation function generators between layers (i.e. variable resistors whose resistance vary non-linearly with the input current).

Domain walls' motion in a magnetic wire is a function of applied current due to spin-orbit torque from an adjacent heavy metal (Fig. 1). The current density and spin orbit torque can be modified along the wire by adjusting the width of the heavy metal. The spin orbit torque then becomes a function of the domain wall position, which makes the domain wall motion a nonlinear function of the applied current (Fig. 2). Linear and nonlinear domain wall motion can be detected via magnetoresistance by using a magnetic tunnel junction in which the magnetic wire forms the free layer. The electrical detection is necessary for the analog matrix multiplication in neuromorphic accelerator. However, domain walls are pinned due to the magnetostatic energy minima on the sides of the MTJ. The synaptic (Fig. 3) and activation function (Fig 4) like magnetoresistive behavior can still be generated by using multiple MTJs in parallel. In this study, we demonstrate linear and nonlinear domain wall motion in magnetic wires and modify the design of magnetic tunnel junctions to convert these motions into magnetoresistance. The experimental observations of the device characteristics agree with both analytical and micromagnetic modeling.

[1] J. A. Currivan-Incorvia, S. Siddiqui, S. Dutta, E. R. Evarts, J. Zhang, D. Bono, C. A. Ross, and M. A. Baldo, Nat Commun., 7, 10275 (2016).

[2] Stuart S. P. Parkin, Masamitsu Hayashi, and Luc Thomas, Science, Vol. 320, Issue 5873, pp. 190-194 (2008)

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2:20pm **EM+PS+TF-MoA3 Ferroelectric Devices for Non-von Neumann Computing**, ***Zheng Wang**, A. Khan,* Georgia Institute of Technology **INVITED**

Excitation and inhibition go hand in hand in neuronal circuits in biological brains. For example, neurons in the visual and the auditory cortices provide excitatory responses to visual and auditory stimuli, respectively. On the other hand, interneurons in the central nervous system provide inhibitory signals to downstream neurons thereby imparting regulation and control in neuronal circuits—the loss of which often causes neurodegenerative disorders. These neuro-biological facts have inspired the bio-mimetic computational perspective that artificial, excitatory neurons need to be paired with inhibitory connections for functional correctness and efficient compute models such as spiking neural networks.

In this talk, we will introduce a ferroelectric neuromorphic transistor platform [1,2] which can (1) efficiently incorporate both excitatory and inhibitory inputs in the simple two transistor topology of an artificial, ferroelectric spiking neuron, and (2) emulate several classes of biological spiking dynamics (such as regular, fast, Thalamo-Cortical spiking and so on). We will discuss the recent experimental demonstrations of ferroelectric spiking neurons. The talk will end with a simulation experiment where a full-scale spiking neural network was implemented using experimentally calibrated ferroelectric circuit models and the network was benchmarked analog CMOS and other emerging device technologies.

References:

[1] Z. Wang, B. Crafton, J. Gomez, R. Xu, A. Luo, Z. Krivokapic, L. Martin, S. Datta, A. Raychowdhury, A. I. Khan, "Experimental Demonstration of Ferroelectric Spiking Neurons for Unsupervised Clustering," *The 64th International Electron Devices Meeting (IEDM 2018)*, 2018.

[2] Z. Wang, S. Khandelwal & A. I. Khan, "Ferroelectric oscillators and their coupled networks," IEEE Electron Dev. Lett. 38, 1614 (2017).

3:00pm **EM+PS+TF-MoA5 Ultrafast Measurement of Nanoseconds Polarization Switching in Ferroelectric Hafnium Zirconium Oxide**, ***Mengwei Si**, P. Ye,* Purdue University

Ferroelectric (FE) hafnium oxides (HfO_2) such as hafnium zirconium oxide (HZO) is the promising thin film ferroelectric material for non-volatile memory applications. The ultrafast measurements of polarization switching dynamics on ferroelectric (FE) and anti-ferroelectric (AFE) hafnium zirconium oxide (HZO) are studied, with the shortest electrical pulse width down to as low as 100 ps. The transient current during the polarization switching process is probed directly. The switching time is determined to be as fast as 10 ns to reach fully switched polarization with characteristic switching time of 5.4 ns for 15 nm thick FE HZO and 4.5 ns for 15 nm thick AFE HZO by Kolmogorov−Avrami−Ishibashi (KAI) model. The limitation by parasitic effect on capacitor charging is found to be critical in the correct and accurate measurements of intrinsic polarization switching speed of HZO. The work is in close collaborations with Xiao Lyu, Wonil Chung, Pragya R. Shrestha, Jason P. Campbell, Kin P. Cheung, Haiyan Wang, Mike A. Capano and was in part supported by SRC and DARPA.

3:20pm **EM+PS+TF-MoA6 Interfacial Charge Engineering in Ferroelectric-Gated Mott Transistors**, *XG. Chen, Y. Hao, L. Zhang, **Xia Hong**,* University of Nebraska-Lincoln

Ferroelectric field effect transistors (FeFETs) built upon Mott insulator channel materials have been intensively investigated over the last two decades for developing nonvolatile memory and logic applications with sub-nanometer size scaling limit. However, the intrinsically high carrier density of the Mott channel (10^{22}-10^{23}/cm^3) also imposes significant challenges in achieving substantial modulation of the channel conduction. In this work, we exploit the intricate interplay between interfacial charge screening and transfer effects in epitaxial heterostructures composed of two strongly correlated oxide layers, one layer of rare earth nickelate $R\text{NiO}_3$ (R = La, Nd, Sm) and one layer of (La,Sr)MnO_3 (LSMO), to realize a giant enhancement of the ferroelectric field effect in Mott-FeFETs with a Pb(Zr,Ti)O_3 gate. For devices with 1-5 nm single layer $R\text{NiO}_3$ channels, the room temperature resistance switching ratio $(R_{off}-R_{on})/R_{on}$ increases with decreasing channel thickness till it reaches the electrical dead layer thickness. For devices built upon $R\text{NiO}_3$/LSMO bilayer channels, the resistance switching ratio is enhanced by up to two orders of magnitude compared with the single layer channel devices with the same channel thickness. Systematic studies of the layer thickness dependence of the field effect show that the LSMO buffer layer not only tailors the carrier density profile in $R\text{NiO}_3$ through interfacial charge transfer, but also provides an extended screening layer that reduces the depolarization effect in the ferroelectric gate. Our study points to an effective strategy for building high density nanoelectronic and spintronic applications via functional complex oxide heterointerfaces.

4:00pm **EM+PS+TF-MoA8 The Interface of Transition Metal Dichalcogenides and Ferroelectric Oxides**, ***Maria Gabriela Sales**, S. Jaszewski, S. Fields, R. Christopher, N. Shukla, J. Ihlefeld, S. McDonnell,* University of Virginia

Transition metal dichalcogenides (TMDs) are an interesting class of materials because of their unique properties owing to their 2D nature, wherein layers that are covalently bonded in-plane are held together by van der Waals forces in the out-of-plane direction, similar to graphene. However, unlike graphene, semiconducting TMDs have a band gap that is tunable with layer thickness, allowing control over its properties depending on specific applications. One such application is in ferroelectric-based transistors, which have high potential for use in memory and logic, but whose major drawback in integration is the poor semiconductor-ferroelectric interface when using silicon as the semiconducting channel, due to issues such as interdiffusion across the interface. Thus, a promising alternative route is using a TMD as the channel with a ferroelectric material as the gate dielectric. This is expected to have an improved interface

quality because of the fact that TMDs have no dangling bonds at the surface and are highly stable in-plane. In this study, we focus on a mixture of hafnium oxide and zirconium oxide as our ferroelectric material, with zirconium stabilizing the ferroelectric phase in hafnia. We explore the TMD/ferroelectric structure, addressing certain integration issues in growth, and looking at their interface chemistry and thermal stability. Specifically, we look at commercially available geological MoS_2 and molecular beam epitaxy-grown WSe_2 interfaced with an atomic layer deposited $Hf_xZr_{1-x}O_2$ ferroelectric. Our report will focus on the results of our investigations of this interface carried out using a combination of X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) techniques.

4:20pm **EM+PS+TF-MoA9 Electronic and Thermal Properties of 2D Materials***, **Connor McClellan**, E. Yalon, K. Smithe, C. English, S. Vaziri, C. Bailey, A. Sood, M. Chen, E. Pop,* Stanford University

This talk will present recent highlights from our research on two-dimensional (2D) materials and devices including graphene, 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.

Using the low cross-plane thermal conductance, we found unexpected applications of graphene as an ultra-thin electrode to reduce power consumption in phase-change memory [1]. We have also demonstrated wafer-scale graphene systems for analog dot product computation [2]. We have grown monolayer 2D semiconductors by chemical vapor deposition over cm^2 scales on amorphous oxides, including MoS_2 with low device variability [3], WSe_2, and $MoSe_2$.

Using a self-aligned process, we demonstrated 10 nm gate-length monolayer MoS_2 transistors with excellent switching characteristics and approaching ballistic limits [4]. Using sub-stochiometric oxides, we achieved high electron doping to reduce electrical contact resistance down to 480 Ω·µm and increase on-current up to a record of 700 µA/µm in monolayer MoS_2 [5]. We also directly measured the saturation velocity in monolayer MoS_2, finding it is thermally-limited (i.e. by device self-heating and phonon scattering) to about one-third that of silicon and about one-tenth that of graphene [6]. 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 [7]. We are presently exploring unconventional applications including thermal transistors [8], which could enable nanoscale control of heat in "thermal circuits" analogous with electrical circuits. These studies reveal fundamental limits and new applications of 2D materials, taking advantage of their unique properties.

References: [1] A. Behnam et al., Appl. Phys. Letters. 107, 123508 (2015). [2] N. Wang et al., IEEE VLSI Tech. Symp., Jun 2016, Honolulu HI. [3] K. Smithe et al., ACS Nano 11, 8456 (2017). [4] C. English et al., IEEE Intl. Electron Devices Meeting (IEDM), Dec 2016. [5] C. J. McClellan et al., IEEE Device Research Conference (DRC), June 2017. [6] K. Smithe et al., Nano Lett. 18, 4516 (2018). [7] E. Yalon, E. Pop, et al., Nano Lett. 17, 3429 (2017). [8] A. Sood, E. Pop et al. Nature Comm. 9, 4510 (2018).

4:40pm **EM+PS+TF-MoA10 Electronics in Flatland***, **Sanjay Banerjee**,* University of Texas at Austin **INVITED**

2D materials such as graphene, transition metal dichalcogenides and topological insulators have opened up avenues in beyond-CMOS device concepts. We will discuss our work involving single or many-particle 2D-2D tunneling, leading to transistors with negative differential resistance. We also explore spintronics in these systems for novel logic and memory devices. We will also discuss the use of these materials in less esoteric, but more practical high frequency, mechanically flexible FETs for IoT applications.

Plasma Science and Technology Division
Room B130 - Session PS+AS+EM+SS+TF-MoA

Plasma-Surface Interactions

Moderators: Sebastian Engelmann, IBM T.J. Watson Research Center, Sumit Agarwal, Colorado School of Mines

2:00pm **PS+AS+EM+SS+TF-MoA2 Plasma Resistance of Sintered Yttrium Oxyfluoride (YOF) with Various Y, O, and F Composition Ratios***, **Tetsuya Goto**, Y. Shiba, A. Teramoto,* Tohoku University, Japan*; Y. Kishi,* Nippon Yttrium Co., Ltd, Japan*; S. Sugawa,* Tohoku University, Japan

Yttrium oxyfluoride (YOF) has been received much attention as the material for various functional components used in the plasma process chamber for semiconductor manufacturing. This is because, as compared to the widely used Y_2O_3, YOF is stable against various corrosive plasmas using halogen gases which is frequently used in the etching processes and/or chamber cleaning processes. We have reported that YOF (1:1:1) film has the higher resistance to various 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 effect of ion bombardment on the surface structure of sintered yttrium oxyfluoride (YOF) with various Y, O, and F composition ratios. By combining the starting materials of YOF, $Y_5O_4F_7$, and YF_3 in sintering, the YOF samples with different Y, O, and F composition ratios were prepared. In these samples, the oxygen composition ratio was changed from 33 at% to 7at%. According to this, the fluorine composition ratio was changed from 33at% to 66at%, and thus, the samples became from Y_2O_3 rich to YF_3 rich. Ar ion beam with 500 eV was irradiated to these YOF samples. It was found that the sputtering etching rate was monotonically decreased as the oxygen composition ratio was decreased. It was also found that the surface roughness was relatively smaller for the samples with the composition ratios of Y:O:F=1:1:1 and 5:4:7 (both correspond to the stable composition) than those with other composition ratios. The results indicated that the atomic composition ratio is an important parameter to obtain YOF with good stability against plasmas.

Acknowledgement

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

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2. A. Teramoto, Y. Shiba, T. Goto, Y. Kishi and S. Sugawa p. 16, AVS 65th International Symp., Long Beach, 2019.

2:20pm **PS+AS+EM+SS+TF-MoA3 Understanding Atomic Layer Etching: Thermodynamics, Kinetics and Surface Chemistry***, **Jane P. Chang**[1],* University of California, Los Angeles **INVITED**

The introduction of new and functionally improved materials into silicon based integrated circuits is a major driver to enable the continued down-scaling of circuit density and performance enhancement in analog, logic, and memory devices. The top-down plasma enhanced reactive ion etching has enabled the advances in integrated circuits over the past five decades; however, as more etch-resistive materials are being introduced into these devices with more complex structures and smaller features, atomic level control and precision is needed in selective removal of these materials. These challenges point to the growing needs of identifying and developing viable etch chemicals and processes that are more effective in patterning complex materials and material systems such as multiferroics, magnetic materials and phase change materials, with tailored anisotropy and selectivity.

In this talk, a universal chemical approach is presented, combining thermodynamic assessment and kinetic validation to identify and validate the efficacy of various plasma chemistries. Specifically, potential reactions between the dominant vapor phase/condensed species at the surface are considered at various temperatures and reactant partial pressures. The volatility of etch product was determined to aid the selection of viable etch chemistry leading to improved etch rate of reactive ion etching process. Based on the thermodynamic screening, viable chemistries are tested experimentally to corroborate the theoretical prediction. Some of the above mentioned material systems such as complex oxides and metallic material systems used in logic and memory devices are used as examples to demonstrate the broad applicability of this approach.

[1] **PSTD Plasma Prize Winner**

3:00pm **PS+AS+EM+SS+TF-MoA5 Comparison of Silicon Surface Chemistry between Photo-Assisted Etching and Ion-Assisted Etching**, ***Emilia Hirsch**, L. Du, V.M. Donnelly, D.J. Economou,* University of Houston

Etching of p-Si in 60 mTorr Cl_2/Ar Faraday-shielded inductively coupled plasmas was investigated under both ion-assisted etching (IAE) and photo-assisted etching (PAE) conditions. Real-time etching rate and after-etch Si surface chemical composition were characterized by laser interferometry and vacuum-transfer X-ray photoelectron spectroscopy (XPS), respectively. By varying the duty cycle of a pulsed negative DC bias applied to the sample stage, it was found that the IAE rate scaled with the ion current integrated over the bias period, and the total etching rate was simply the sum of PAE and IAE rates. Consequently, little or no synergism occurred between VUV photon- and ion-bombardment stimulated etching. The PAE rate was ~ 210 nm/min at 60 mTorr. Above the 25 eV threshold, the IAE etching rate increased with the square root of the ion energy. Compared to RF bias, a more monoenergetic IED was obtained by applying pulsed DC bias, allowing precise control of ion energy near the low-energy IAE threshold. XPS spectra showed that, when compared to IAE, the chlorinated layer on the surface of samples etched under PAE conditions had significantly lower chlorine content, and it was composed of SiCl only. Under IAE conditions, however, Si· dangling bonds, $SiCl_2$, and $SiCl_3$ were found, in addition to SiCl, with relative abundance of SiCl>$SiCl_2$>$SiCl_3$. The absence of higher chlorides and Si· dangling bonds under PAE conditions suggested that VUV photons and ions are interacting with the Si surface very differently. When PAE and IAE occurred simultaneously, energetic ion bombardment dictated the surface chemistry that resulted in the formation of higher chlorides.

3:20pm **PS+AS+EM+SS+TF-MoA6 Chemical Reaction Probabilities in the Etching of Si by Fluorine Atoms Produced in a Mixture of NF-$_3$/SF_6 Plasma**, ***Priyanka Arora**[1], T. Nguyen,* University of Houston*; S. Nam,* Samsung Electronic Company, Republic of Korea*; V.M. Donnelly,* University of Houston

Reaction probabilities in the absence of ion bombardment, defined as the number of silicon atoms removed per incident fluorine atom, have been investigated in mixtures of NF_3 and SF_6 plasmas in an inductively-coupled plasma reactor. Fluorine atom densities were measured by optical emission actinometry, and isotropic etching rates were measured by the degree of undercutting of SiO_2-masked silicon, using cross-sectional scanning electron microscopy (SEM). In addition, atomic force microscopy (AFM) was used to examine surface roughness after etching. The F atom reaction probabilities derived from these measurements indicate ~30-fold higher reaction probability in SF_6 plasma compared with values in NF_3 plasma. Surfaces etched in SF_6 plasma were much smoother than those etched in NF_3 plasma. Addition of only 10% SF_6 to an NF_3 plasma produced a much higher reaction probability (~10-fold) than in a pure NF_3 plasma. This surprising enhancement of reaction probabilities for F with Si in SF_6 plasma will be shown to be due to adsorbed sulfur acting as a catalyst to greatly enhance the etching rate of Si. By allowing sulfur in isopropyl alcohol to evaporate on the masked Si samples, sulfur could be preferentially deposited in relatively high concentrations near mask edges in ~2 mm diameter periodic "strings of beads". When this sample is placed side by side with one not exposed to sulfur, the sulfur dosed sample etched several times faster at the center of each bead, while sulfur-free surface exhibited the expected slower rate.

4:00pm **PS+AS+EM+SS+TF-MoA8 John Thornton Memorial Award Lecture: Low Temperature Plasma-Materials Interactions: Foundations of Nanofabrication And Emerging Novel Applications At Atmospheric Pressure**, ***Gottlieb S. Oehrlein**[2],* University of Maryland, College Park **INVITED**

Our ability to understand and control the interactions of non-equilibrium plasma with surfaces of materials has been an exciting frontline and enabled the realization of new applications and technologies. The plasma-surface interactions (PSI) field has grown rapidly because of a number of reasons. First, plasma-assisted etching (PE) is one of the foundations of micro- and nanofabrication where increasingly atomistic precision in materials processing is required. By enabling the realization of intricate material features that semiconductor circuits and microstructures consist of, PE makes possible our technological tools that form modern society. This exceedingly complex procedure begins with the transfer of a resist mask in a directional and chemically selective fashion into various materials. Controlling profile shape, critical dimensions, surface roughness, and electrical integrity are crucial, and determined by PSI. Second, development of novel low temperature plasma sources operating at atmospheric pressure has enabled advances in areas where use of PSI has historically been limited, e.g. biology. In this talk I will present a brief review of contributions that I and my collaborators have been honored to make to our understanding of PSI, in particular in the areas of surface processes that are essential for achieving the objectives of plasma etching processes in current semiconductor fabrication that are approaching the atomic scale, and interaction of low temperature atmospheric pressure plasma sources with model polymers and biomolecules aimed at disinfection and sanitation of biological materials.

4:40pm **PS+AS+EM+SS+TF-MoA10 Determining Surface Recombination Probabilities during Plasma-enhanced ALD using Lateral High Aspect Ratio Structures**, ***Karsten Arts**,* Eindhoven University of Technology, The Netherlands, Netherlands*; M. Utriainen,* VTT Technical Research Centre of Finland, Finland*; R.L. Puurunen,* Aalto University School of Chemical Engineering, Finland*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; H.C.M. Knoops,* Eindhoven University of Technology, The Netherlands

In this work we measure surface recombination probabilities r of plasma radicals, which is essential for the modeling and understanding of radical-driven plasma processes. Such quantitative information on r is scarcely reported in the literature and typically obtained by difficult and indirect measurement techniques. Here, we determine r using plasma-enhanced atomic layer deposition (ALD) on high aspect ratio (AR) structures, where the AR up to which film growth is obtained gives direct insight into r corresponding to the growth surface. This is demonstrated by measuring the recombination probabilities of O atoms on SiO-$_2$, TiO_2, Al_2O_3 and HfO_2, revealing a surprisingly strong material-dependence. Aside from studying different materials, our method can for instance be used to investigate the impact of pressure and temperature on r. This can provide valuable information for e.g., device fabrication, plasma source design and simulations, in the context of plasma-enhanced ALD but also relevant outside this field.

For this study, we use microscopic lateral-high-aspect-ratio (LHAR) structures[1] supplied by VTT (PillarHall® LHAR4). These chips have extremely high AR trenches (AR<10000) such that film growth is limited up to a certain penetration depth for even the most conformal processes. In the case of plasma ALD, where the film conformality is typically limited by surface recombination,[2] we show that the achieved penetration depth can be used to determine r. Furthermore, the LHAR structures allow for comparison of growth behavior with and without an ion component.

These opportunities are demonstrated by plasma ALD of SiO-$_2$, TiO_2, Al_2O_3 and HfO_2, using an O_2/Ar plasma and $SiH_2(N(C_2H_5)_2)_2$, $Ti(N(CH_3)_2)_4$, $Al(CH_3)_3$ and $HfCp(N(CH_3)_2)_3$, respectively, as precursors. It is observed that an exponential increase in plasma exposure time is required to linearly increase the film penetration depth. This relation, which solely depends on r, has been used to determine $r=(6\pm2)\cdot 10^{-5}$, $(6\pm3)\cdot 10^{-5}$, $(1\text{-}10)\cdot 10^{-3}$ and $(0.1\text{-}10)\cdot 10^{-2}$ for oxygen radicals on SiO-$_2$, TiO_2, Al_2O_3 and HfO_2, respectively. Corresponding to these large differences in r, growth of SiO_2 and TiO_2 penetrated extremely deep up to AR~900, while deposition of Al_2O_3 and HfO_2 was achieved up to AR~90 and AR~40, respectively. This strong material-dependence illustrates the importance of our quantitative research on surface recombination of plasma radicals.

1. Arts, Vandalon, Puurunen, Utriainen, Gao, Kessels and Knoops, J. Vac. Sci. Technol. A **37**, 030908 (2019)
2. Knoops, Langereis, van de Sanden and Kessels, J. Electrochem. Soc. **157**, G241 (2010)

5:00pm **PS+AS+EM+SS+TF-MoA11 Study of Plasma-Photoresist Interactions for Atomic Layer Etching Processes**, ***Adam Pranda**[3], K.-Y. Lin, G.S. Oehrlein,* University of Maryland, College Park

The emergence of atomic layer etching (ALE) processes has enabled improved control of surface profiles. Whereas the implementation of ALE processes on hard mask materials has been well established, the effects of these processes on photoresist materials is not well known. With the advent of next generation extreme ultraviolet (EUV) photoresists, there is the potential to utilize ALE processes with photoresist materials for fabrication of sub-10 nm feature sizes.

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

[2] **John A. Thornton Memorial Award Winner**

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

The plasma processing of photoresist materials induces several key physical and chemical modifications which affect material properties such as the etching behavior and surface roughness. In this work, we utilize in-situ ellipsometry, atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy to interpret the relationships between the aforementioned material properties, the photoresist chemical composition, and plasma ALE parameters such as ion energy and precursor gas type. By comparing these relationships between baseline continuous plasma etching processes and ALE processes, which include the introduction of chemically reactive surface passivation, we elucidate the intrinsic photoresist behaviors under plasma exposure and how an ALE process specifically impacts these behaviors.

Under nonreactive plasma chemistries, a universal response among photoresist materials is the development of a surface dense amorphous carbon (DAC) layer due to energetic ion bombardment. We have found that the photoresist etch rate is inversely proportional to the DAC layer thickness.[1] However, photoresists with UV sensitive pendant groups, such as 193 nm photoresists, develop a greater surface roughness due to the stresses in the surface generated by synergistic ion and UV photon interactions.

With depositing fluorocarbon (FC)-based ALE gas chemistries, the deposited FC layer reacts with the DAC layer and converts it into a mixed layer. This incorporation of FC into the DAC layer reduces the surface roughness without impacting the etch rate of the underlying photoresist as long as a sufficient DAC layer thickness remains.[2] This behavior is potentially advantageous for maximizing the photoresist to SiO_2 selectivity while maintaining an adequate surface roughness.

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Plasma Science and Technology Division
Room B131 - Session PS1-MoA

Plasma-Liquid Interactions, Medicine, and Agriculture

Moderators: Kazunori Koga, Kyushu University, Japan, Deborah O'Connell, University of York, UK

1:40pm **PS1-MoA1 Peroxynitric acid ($HOONO_2$) Chemistry in Plasma-treated Water for Effective and Safety Disinfection*, Katsuhisa Kitano,*** Osaka University, Japan*; S. Ikawa, Y. Nakashima,* Osaka Research Institute of Industrial Science and Technology, Japan*; T. Yokoyama,* Osaka University, Japan*; A. Tani,* Kobe University, Japan **INVITED**

Plasma medicine is one of attractive research areas in the area of plasma application. By the exposure of low temperature atmospheric plasma to living organism (human body, bacteria, and so on), positive effect is expected. As biological environment is wet condition, plasma induced chemical reactions in liquid should be considered.

For the plasma disinfection of human body, we have developed the reduced-pH method with direct plasma exposure, which brings stronger bactericidal activity in the liquid at lower pH condition, where the threshold is pH 4.8. The enhancement is thought to be due to hydroperoxy radical (HOO•) generated from superoxide anion radical (O_2^-•) by acid dissociation equilibrium (pKa 4.8). Electrically neutral HOO• could easily penetrate into cell to bring intracellular oxidative stress. In addition, we found that the plasma-treated water (PTW) also has strong bactericidal activity under acidic condition in the same manner. Physicochemical properties of PTW are discussed based on chemical kinetics. Lower temperature brings longer half-life, and the bactericidal activity of PTW can be kept by cryo-preservation. This means that PTW with higher bactericidal activity could be obtained by longer plasma treatment under enough low temperature. High performance PTW, corresponding to the disinfection activity of 22 log reduction (against Bacillus subtilis spore), can be obtained by special plasma system equipped with cooling device. The bactericidal activity of our PTW is much stronger than others.

Many researchers are interested in this area of PTW, where the waters are treated / activated by their original devices. For scientific understanding, we should discuss based on chemical species. Although PTW has many chemical components, respective chemical components in PTW were isolated by ion chromatography. Active ingredient of PTW was successfully purified to be confirmed to $HOONO_2$ (PNA: peroxynitric acid). Although the existence of PNA has been known since 100 years ago, sterilization by PNA has never been reported in past papers. PNA is known to release HOO• by radical cleavage. So we conclude that PNA is a key chemical species of cryo-preserved PTW with the reduced-pH method.

From the experimental results of chemical synthesis, PNA is effectively generated from HNO_2 and H_2O_2 under extremely acid condition (pH < 2). Although averaged pH of PTW is about 3~4, pH at the surface of PTW (limited area of interface between plasma and liquid) during plasma treatment is thought to be enough low that PNA can be synthesized from HNO_2 and H_2O_2 supplied from plasma. In the presentation, peroxynitric acid chemistry in PTW will be discussed in detail.

2:20pm **PS1-MoA3 Impact of Solution Properties on Plasma Formation in DC Plasma Electrolysis*, Hernan E. Delgado***[1]*, D.M. Bartels, P. Rumbach, D.B. Go,* University of Notre Dame

A common configuration used in plasma-liquid interactions is that in which a direct current (DC) gas discharge is generated between a liquid and a metal. Under this configuration, known as plasma electrolysis or glow-discharge electrolysis, the liquid itself functions as a plasma cathode or anode, for a positive or negative DC bias, respectively. However, it is not clear exactly how the liquid participates in the formation and sustaining of the plasma, including charge transfer at the plasma-liquid interface. This is especially true when the liquid is acting as a cathode, and secondary emission from the liquid is ostensibly required to sustain the plasma. In this work, we use measurements of the breakdown and discharge voltages to understand this process. Voltage measurements for an argon plasma in contact with an aqueous solution are conducted in an electrochemical H-cell reactor to test for conditions that would facilitate secondary emission from the liquid. Voltage measurements across the plasma show a strong dependence on ionic strength, and no dependence on pH (from pH = 0 to 14) while controlling for ionic strength. The voltage was also found to be strongly dependent on the temperature of the liquid. Free radical scavengers nitrite and nitrate had no significant effect on the plasma voltage even at 1.0 M concentration, suggesting that the solvated electron, the pre-solvated electron, and the hydrogen atom do not play a crucial role in secondary emission as previously proposed.

2:40pm **PS1-MoA4 Plasma Reactive Species Formation in Liquids*, Sylwia Ptasinska,*** University of Notre Dame **INVITED**

Plasma reactive species which are directly originated in an atmospheric pressure plasma jet (APPJ) and/or indirectly produced in liquids can drive a plethora of chemical reactions. Despite the rapid growth in interest in this type of plasma, our fundamental and comprehensive knowledge of the chemistry which plasma induces in multiphase systems is still needed to be achieved. One of the approaches to obtain this goal is a development of sophisticated interrogation techniques to provide such characterization. In our laboratory, we developed in situ optical absorption technique, and used ferrous sulfate (Fricke) solution in which species were detected under plasma interaction to quantify the total yield of these species under different experimental conditions. A yield of ferric (Fe3+) ions measured using this technique was attributed to the formation of plasma reactive species provided and/or originated in the solution. The results indicated that the number of reactive species formed was proportional to plasma frequency and voltage. However, the Fe3+ yield per pulse decreased with increased frequency. To obtain a better understanding of the processes and species involved in the chemical reactions due to plasma exposure, Fe3+ yields were calculated and compared to the experimental data. At higher frequencies, there was insufficient time to complete all reactions before the next pulse reached the solution; at lower frequencies, the Fe3+ yield was higher because of the relatively longer time available for reactions to occur. It is also known that gas composition of APPJ as well as ambient conditions influence plasma chemistry and thus also reactions in liquids which are in contact with plasma. We performed systematic studies to probed changes in plasma electrical properties, by adjusting the fraction of oxygen and water vapor in the plasma jet environment and feed gas. While DNA was used to identify chemical changes that occurred in the plasma jet under these various experimental conditions. We determined optimal conditions at which increase in the damage to the molecular probe was significant. This increase can be attributed primarily to the formation of reactive species caused by water and oxygen decomposition in the APPJ.

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

At the same time, we observed no change in the plasma electrical power when oxygen or water vapor were added to the jet environment but decreased when these gases were introduced to the feed gas. This indicates that the effects of plasma chemistry supersede those due to the power applied for APPJ ignition.

3:20pm **PS1-MoA6 In-flight Synthesis and Online Characterization of Silver Nanoparticles from Aerosol Droplets Reacting in a Non-thermal Plasma***, **Tommaso Gallingani,*** Alma Mater Studiorum-University of Bologna, Italy, Italia*; N.H. Abuyazid,* Case Western Reserve University*; M. Gherardi, V. Colombo,* Alma Mater Studiorum-University of Bologna, Italy*; C.J. Hogan,* University of Minnesota, Minneapolis*; R.M. Sankaran,* Case Western Reserve University

Because of their unique features and low-temperature chemistry, non-thermal, atmospheric-pressure (AP) plasmas have attracted interest for material synthesis in multiphase environments where the plasma is in contact with a liquid surface. In the most common configuration, the reaction interface is highly localized, leading to inhomogeneities and mass transport limitations. In light of these issues, liquid water jet and a liquid aerosol have been proposed as alternative strategies that allow continuous liquid flow and promote more controlled reaction. However, applications of these multiphase systems are complicated and limited by lack of knowledge of reaction mechanisms.

Here, we carried out a detailed study of a flow-through, liquid-droplet plasma system using an online ion mobility spectrometry (IMS) system to characterize precursor to particle conversion. IMS measures the electrical mobility of aerosol particles providing real time size distribution. The focus of our study was silver nitrate ($AgNO_3$) which has been well-studied in plasma-liquid synthesis and, thus, provides a straightforward chemistry to benchmark our results . Liquid droplets containing $AgNO_{-3}$ were produced by a Venturi effect nebulizer and carried in by an argon flow into an AP dielectric barrier discharge (DBD). The DBD configuration was a quartz tube with two ring electrodes in parallel to avoid any metal in contact with the plasma and driven by an alternating current high voltage generator. The effluent of the reactor was diluted by a flow of nitrogen gas and coupled to the inlet of a commercial IMS system. For a given flow rate, precursor concentration, and plasma power, our results show that the mean particle diameter decreases from 38 to 26 nm when the plasma is on which could be ascribed to $AgNO_3$ reduction to silver (Ag). The synthesized Ag nanoparticles (NPs) were collected either by electrostatic precipitation or filtration for materials analysis. NPs size distribution and morphology were assessed by transmission electron microscopy and found to have good agreement with IMS data. Ultraviolet-visible absorbance showed the well-known localized surface plasmon resonance peak for Ag at approximately 400 nm, confirming a successful conversion. We also performed a control experiment with a diffusion dryer to remove the water and only introducing dried $AgNO_3$. The lack of any reduction to Ag NPs suggested that the mechanism involves water and plasma species alone cannot reduce $AgNO_3$. This study provides important insight into liquid-droplet-based multiphase plasma reactors which are a novel approach to synthesizing NPs from precursors that are not available as a vapor.

4:00pm **PS1-MoA8 Plasma-assisted Fabrication and Functionalization of Materials for Applications at the Nano-biointerface***, **Cristina Satriano,*** University of Catania, Italy **INVITED**

Surface tailored (nano)materials are of striking interest to better control protein/material and cell/material interactions at the sub-molecular level.

Current fabrication of nanomaterials is facing the following two challenges: high selectivity toward specific chemical compositions or morphologies and their scalable production. This usually requires new synthesis/functionalisation conditions beyond the conventional approaches.

Plasma chemistry presents an opportunity to explore these features and to potentially trigger new surface-driven biological effects. Indeed, the unique synergy of physical and chemical phenomena that occur in the low temperature plasmas has led to an ever-increasing effort to find solutions to currently problematic medical, agricultural, cosmetic and environmental problems by using multifaceted cold plasma environment.

In this paper, the latest progress in the plasma-assisted fabrication and/or functionalization of materials from nanoparticles to low-dimensional nanostructures, including graphene oxide, are briefly reviewed, with a special focus on discussing plasma properties responsible for the nanomaterial growth with high throughput, desired compositions and shapes, or narrow size distributions as well as for the surface functionalization with some control on the ageing processes.

Case studies on plasma-synthesized plasmonic nanogold and nanosilver with tunable optical and electrical properties and plasma surface-modified polymers and nanocarbons at the interface with peptides/proteins, extracellular matrix, supported lipid bilayers and cells are discussed. An outlook of challenges and opportunities for further advancement in this emerging field is given.

4:40pm **PS1-MoA10 Cold Plasma Jets, Liquids and Biomaterials for Bone Cancer Therapy***, **Cristina Canal,*** Universitat Politècnica de Catalunya, Spain **INVITED**

Over the last few years, significant attention has been paid to biomedical applications of Atmospheric Pressure Plasmas (APP), and especially to the involvement of reactive species (RONS) in selective cancer cell death [1] without damaging surrounding healthy tissues [2]. The anti-cancer properties of the APP have been described in many cancer cell lines, such as breast, skin, lung, pancreas, brain cancers among others and only more recently in bone cancer cells [3-4]. The biological effects of plasmas have been observed also in a wide variety of plasma activated liquids (PAM) [5], opening the door for minimally invasive therapies.

Despite being rare, Osteosarcoma (OS) is the most common primary bone tumorbeing the most common solid tumor in teenagers and the third most common malignancy in children. Our research focuses on the effects of plasmas on osteosarcoma.

We have investigated the effects of different plasma jets in the generation of RONS in liquids of biological interest. OS cells show higher sensitivity to PAM treatment than healthy cells, activating apoptosis, DNA damage and deregulating cellular pathways mediated by c-JUN, AKT, AMPK or STAT3 [6].

However, injection of a liquid in the body associates it being washed away by the blood flow, so development of efficient vehicles which allow location and delivery of RONS to the diseased site is lacking. Therefore, it is our interest to elucidate the potential of hydrogels to generate and store RONS generated by plasmas. Hydrogels are highly hydrated networks of cross-linked polymer chains whose features such as biocompatibility make them great candidates for the design of advanced biomaterials.

We will discuss different hydrogels; in general, their physic-chemical properties remain unchanged by the plasma treatment, while the hydrogels show several-fold larger capacity for generation of RONS than a typical PAM – the absolute amounts generated depending a lot on the chemistry of the hydrogel. The hydrogels show different capacity for release of RONS depending on their properties. The plasma-treated hydrogels show efficient killing of OS cells, related to the different RONS generated.

Acknowledgement. This project has received funding from ERC under the European Union’s Horizon 2020 research and innovation programme (grant agreement No714793).

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Electronic Materials and Photonics Division
Room A214 - Session EM+2D+AP+NS+PS-TuM

New Devices and Materials for Electronics and Photonics

Moderators: Sean W. King, Intel Corporation, Michelle M. Paquette, University of Missouri-Kansas City

8:00am **EM+2D+AP+NS+PS-TuM1 Performance Modeling and Design for Spintronic Logic and Memory Devices***, **Azad Naeemi,*** Georgia Institute of Technology **INVITED**

As scaling conventional logic and memory devices becomes more and more challenging, there is a global search for novel materials and devices that can augment mainstream technologies used for data storage and processing. To this end, spintronic materials and devices are promising candidates as they provide dense non-volatile storing elements that enable novel computing paradigms such as in memory-computing and neural networks.

This talk will present physical models for various read and write spintronic mechanisms and quantifies the potential performances of Boolean circuits based on various spintronic logic devices. It will be shown that without major breakthroughs such circuits will not be able to compete with their CMOS counterparts. However, novel circuit paradigms that take advantage of the physics of these devices can potentially provide significant benefits. For example, cellular neural networks based on spintronic devices are projected to perform better compared to their analog CMOS implementation.

While spin-transfer-torque random access memory (STT-RAM) is becoming commercially available, it suffers from relatively large switching currents that limits its density and causes reliability challenges. Novel read and write mechanisms such as spin-orbit torque or magneto-electric effects can potentially address or partially mitigate some of these challenges. In this talk, the array-level potential performance of various magnetic memory devices will be quantified and benchmarked.

8:40am **EM+2D+AP+NS+PS-TuM3 High Yield, Low Variability HfO_2 1T1R Cells Fabricated in 65nm CMOS***, J.H. Hazra, M.L. Liehr, K. Beckmann, **Nathaniel C. Cady,*** SUNY Polytechnic Institute

Hafnium Oxide (HfO_2) based Resistive Random Access Memory (ReRAM) devices are promising candidates for non-volatile memory, having a wide variety of applications in neuromorphic computing, artificial intelligence and future memory solutions. Stochastic conductive filament (CF) generation and rupture processes, however, contribute to high variability resistive switching in these devices. In order to address this issue, an extensive characterization of HfO_2 1 transistor 1 RRAM (1T1R) cells was performed to investigate switching yield and cell-to cell variability. 1T1R devices were integrated into a 300mm wafer platform utilizing the IBM 65nm 10LPe process technology, in which the memristor device stack is implemented between the M1 and M2 metallization layers, using a custom designed FEOL compatible process flow. The ReRAM device stack is comprised of a TiN bottom electrode followed by conformal deposition of the HfO_2 switching layer, Ti oxygen scavenging layer and TiN top electrode. The HfO_2 switching layer was deposited using an atomic layer deposition (ALD) process with an organic precursor. For statistical significance, the performance of 50 different 1T1R cells was compared for cell-to-cell variability in operating voltage and resistance in the on and off state. An impressive 100% switching yield and low cell-to-cell switching variability were observed for these devices. 1T1R cells were also investigated for long term endurance and high temperature retention, exhibiting excellent endurance of up to 1 billion switching cycles with an average R_{off}/R_{on} ratio of 10:1. As compared to 1T1R cells that we have fabricated with alternative ALD precursors/methods, these devices show superior yield and performance. We are currently performing compositional and structural comparisons between these sets of devices, to elucidate the impact of ALD precursor choice and processing methods on yield and electrical performance.

9:00am **EM+2D+AP+NS+PS-TuM4 Heat Transfer Proximity Effects in Resistive Memory Crossbar Arrays***, **Marius Orlowski,** M.S. Al-Mamun,* Virginia Tech

Evidence for thermal cross talk in resistive RAM memory arrays is presented. Frequent switching of a resistive memory cell ($Cu/TaO_x/Pt$) may lead to a considerable local accumulation of Joules heat. The heat generated in a stressed device spreads via common electrode lines to the neighboring cells impacting their switching behavior. As a probe into degraded performance of the neighbor cells we choose the cell itself set into the on-state under specific conditions. The cell is set at a critical compliance current I_{cc} that allows repeated switching for no more than ~15 cycles. After the maximum number of cycles the on-state becomes volatile. For a lower I_{cc}, the cell produces a volatile on-state, and for higher I_{cc} the cell switches for hundred of times with a stable on-state. We find that the cells in close proximity of the heated device display various degrees of degradation indicated by a reduced number of cycles of the probed cell. The 1st neighbor cell experiences the greatest, and the 4th neighbor cell the smallest degradation. This indicates the spread of the heat from the heated device to its neighbors. After a sufficient cooling off period (10 minutes or longer), all the neighboring cells and the heated device display again the maximum number of cycles i.e. 15, when set under the critical compliance current and reset, repeatedly. Also cells that don't share any of the common electrode metal lines with the heated source cell, may degrade provided that the intermediate cells are set to on-state, thus enabling a continuous thermal conduction path between the heated cell and the probed cell. The heat dissipation from the heated device is slower for narrow and thin metal electrode lines than for wide and thick metal lines. However, in case of wide and thick metal lines more distant neighbor cells are affected by the parasitic cell-to-cell heat transfer.

We have performed the characterization o the neighboring cells along the Cu and Pt electrode lines. We find that the performance degradation of the neighboring cells along the Cu line is significantly stronger than along the Pt metal line. This observation is consistent with the much better heat conductivity of Cu lines (385W/(mK) and 150nm thick) than the Pt (72W/(mK) and 50nm thick) lines, but is at odds with the assumption of the standard electro-chemical metallization model postulating a conical shape of the Cu filament with a broad base of the cone at the Pt electrode and a tip at the Cu electrode. We discuss the extant controversial experimental evidence and models for the filament's shape and propose an hour-glass shape for the filament reconciling the extant findings and our thermal results.

9:20am **EM+2D+AP+NS+PS-TuM5 High Performance Memristive Action in Methylammonium Bismuth Iodide([MA]3Bi2I9) Films***, P. Cheng,* Vanderbilt University*; G. Luo,* Washington University in St. Louis*; Z. Gao,* University of Central Florida*; A. Thind, R. Mishra,* Washington University in St. Louis*; **Parag Banerjee,*** University of Central Florida

We demonstrate high performance (ON/OFF ~ $2.4x10^5$) resistive switching in methylammonium bismuth iodide ($(CH_3NH_3)_3Bi_2I_9$ or, MBI) thin films.[1] MBI has a post-perovskite structure and consists of 2D layers of face-shared

BiI_6 octahedra. This talk focuses on the structure, composition and associated defect chemistry that is critical for memristive behavior in MBI films.

Memristors are formed by contacting MBI films with aluminum electrodes. The switching for a 200 nm film is observed at voltages ~ 0.5 V. High frequency performance of these memristors shows a peak ON/OFF ratio $2.4x10^5$at 50 KHz. The ON state retention is maintained at 50C for > 10^6 seconds. Stable room temperature endurance is noted for up to 1000 cycles. Energy dispersive x-ray spectroscopy on planar memristor devices show that, postswitching,

a detectable change in the I- concentration is observed closer to the anode side. Density-functional theory (DFT) calculations show low activation barrier for iodine migration in agreement with the experimental results. The DFT calculations also provide insights about the migration pathway and strategies to control this behavior.

From a synthesis perspective, MBI films can be deposited using solution as well as low temperature (< 200C), atmospheric CVD technique.[2] The compounds are air stable. This family of ternary compounds offers a large compositional and structural tunability; unlike binary metal oxides commonly used for memristors. As opposed to recent 2D MoS_2 based planar, tunneling RAM devices[3], the vertical stack of the 2-terminal memristor bodes well for scalability. Thus, we propose that hybrid organic-inorganic thin films may offer strategic materials and design advantages together with seamless process integration into current Si-based devices.

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9:40am **EM+2D+AP+NS+PS-TuM6 Mechanism of Chalcogen Passivation of GaAs Surfaces***, **Takayuki Suga**, S. Goto,* UEC-Tokyo, Japan*; A. Ohtake,* NIMS, Japan*; J.N. Nakamura,* UEC-Tokyo, Japan

GaAs surfaces are stabilized by surface treatments with Se or S through the reduction of the dangling bond density [1,2]. It has long been thought that the Se- or S-treated GaAs(111)B-(1x1) surface has a simple structure; the outermost As atoms of the ideal (111)B surface are completely replaced by Se or S atoms, the Se- or S-terminated model [3]. In general, the structural stability of compound semiconductor surfaces can be explained in terms of the so-called electron-counting rule (ECR) [4]. The Se- or S-terminated model, however does not satisfy ECR. Recently, the atomic structure of the Se-treated GaAs(111)B surface has been revisited [5] and another structure model has been proposed, where the Se atoms substitute 3/4 of the topmost surface As atoms in a (2x2) unit [6]. This mixed Se/As-terminated model satisfies ECR, being electronically stable [6]. We have depicted phase diagrams of Se- or S- treated GaAs(111)B surface at 0K as functions of the chemical potentials of Se ($\Delta\mu_{Se(S)}$) and As ($\Delta\mu_{As}$). The (2x2) As-trimer and the mixed Se(S)/As-terminated surfaces appear under Se poor condition. It is noted that the Se- or S-terminated surface also becomes stable as $\Delta\mu_{Se}$ or $\Delta\mu_{S}$ increases, respectively, even though these surfaces are not qualified for ECR.

The Se(S)-treated GaAs(111)B surface is prepared experimentally by molecular beam epitaxy under a finite temperature and a gas pressure. Therefore, it is necessary to consider the free energy of a molecule in vapor phase. In this study, we investigate the stabilization of the Se- or S-treated GaAs(111)B surface structures by considering the beam equivalent pressure of As and Se(S) in a growth temperature using the first-principles calculations within the density functional theory. The chemical potentials of molecules are derived from the partition functions for the translation, the rotation, and the vibrational motions.

In the phase diagram for the actual experiment condition, T=800K, the mixed Se/As terminated surface appears in the Se pressure of 10^{-15}-10^{-5} Torr, being consistent with the recent experiment [5]. Surprisingly, the Se-terminated surface also becomes stable as the Se pressure increases. We will discuss the stabilization mechanism of the chalcogen-treated GaAs surfaces.

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11:00am **EM+2D+AP+NS+PS-TuM10 Combining 2D and 1D Atomic Scale Tailored Nanowire Surfaces for Novel Electronics and Photonics***, **Anders Mikkelsen**,* Lund University, Sweden **INVITED**

The III-V nanowire (NW) technology platform has reached a level of advancement that allows atomic scale control of crystal structure and surface morphology as well as flexible device integration. In particular, controlled axial stacking of Wurtzite (Wz) and Zincblende (Zb) crystal phases is uniquely possible in the NWs. We explore how this can be used to affect electronic, optical and surface chemistry with atomic scale precision opening up for 1D, 2D and 3D structures with designed local properties.

We have previously demonstrated atomically resolved Scanning Tunneling Microscopy/Spectroscopy (STM/S) on a wide variety of these III-V NWs and on operational NW devices[1-4]. We now use these methods for studying atomic scale crystal phase changes, the impact on local electronic properties and demonstrating full atomic resolution STM during device operation[5-7]. We explore the surface alloying of Sb into GaAs NWs with controlled axial stacking of Wz and Zb crystal phases[5] demonstrating a simple processing-free route to 1D and 2D compositional control at the monolayer level. Further we show how Bi can form unique 1D and 2D structures in particular on the unique Wz GaAs NW segments. Using 5K STM/S we measure local density of states of Zb crystal segments in Wz InAs NWs down to the smallest possible atomic scale crystal lattice change [6], which is effectively a small 2D material segment in a 1D structure. We find that the general Zb electronic structure is preserved locally in even the smallest segments and signatures of confined states in them.

Characterization to the atomic scale during electrical and optical operation is necesarry to understand and develop the functionality of structures as discussed above. We demonstrate a novel device platform allowing STM/S with atomic scale resolution across a III-V NW device simultaneously with full electrical operation and high temperature processing in reactive gases[7].Using 5-15 femtosecond laser pulses combined with PhotoEmission Electron Microscopy (PEEM) we explore local dynamic response of carriers in the 1D Wz and Zb crystal phases down to a few femtoseconds temporally and a few tens of nanometer spatially[8].

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11:40am **EM+2D+AP+NS+PS-TuM12 Nanoflower Decorated GaN and AlGaN/GaN based Catalyst-free CO Sensors***, **Monu Mishra**, G. Gupta,* National Physical Laboratory, India

III-Nitride semiconductors owing unique material properties have proven their potential in the detection of light, chemical, biomolecules and toxic/explosive gases. Despite of numerous advantages *viz.* biocompatibility, high temperature/frequency tolerance and harsh/adverse environmental condition sustainability, the use of expensive catalysts (e.g. platinum) and higher operation temperature (>250°C) for gas sensing has plagued the development of GaN based cost-effective sensing technology. Upto the best of our knowledge, literature lacks any scientific report on the development of catalyst-free CO sensors operating at room-temperature using GaN or AlGaN/GaN structures indicating the necessity of dedicated scientific attention in this area. Therefore, we report the fabrication of nanoflowers-decorated GaN and AlGaN/GaN heterostructure based catalyst-free CO sensors operating at lower (including room) temperature. Planar as well as nanostructured GaN & AlGaN/GaN thin films were employed for sensors fabrication which exhibited significant CO sensing associated with its superior surface and interface properties. For in-depth understanding, the obtained results were thoroughly analyzed and correlated to investigate the underlying science/phenomenon which revealed that CO sensing on GaN (and AlGaN/GaN) is governed by the chemical nature of ambient-oxidation induced amorphous oxide (O_2^-, O^{2-} orOH^- species) layer grown on the surface and acting as a donor/acceptor state. Besides, electron accumulation at AlGaN/GaN interface influenced the critical parameters like schottky barrier height, ideality factor etc. perturbed the effective carrier transport and ultimately the device performance. The study demonstrate that development of catalyst-free room temperature operating GaN based CO sensors is feasible using nanostructured surfaces, though further research is required for optimization of device performance.

12:00pm **EM+2D+AP+NS+PS-TuM13 Surface Transfer Doping of Diamond by Complex Metal Oxides for Power Electronics: A Combined Experimental and Simulation Study***, **Vihar Georgiev**, A.J. Moran, A. McGhee,* University of Glasgow, UK

Diamond has unique properties that make it an attractive wide band-gap material to produce future high-performance electronic devices. With a wide band-gap of 5.5eV, a thermal conductivity 5 times greater than 4H-SiC, a high breakdown field and high hole and electron carrier velocities, diamond is a clear stand out candidate for high frequency and high power devices. However, the lack of a suitable doping mechanism has hindered the application of diamond in electronic devices. Conventional substitutional doping techniques are limited as it is difficult to substitute atoms into the diamond crystal lattice.

Surface Transfer Doping (STD) gives the use of diamond for such applications more promise. For STD to occur there are typically two prerequisites: hydrogen terminated diamond (H-diamond) and an electron accepting material in intimate contact with the H-diamond surface. The

hydrogen termination gives the diamond a negative electron affinity which facilitates the transfer of electrons from the diamond to the electron-accepting material, creating a shallow, quasi two-dimensional hole gas (2DHG) in the diamond. This doping process traditionally relies upon interfacial electron transfer between the diamond valence band and favourable energy states provided by atmospheric molecules dissolved in a water layer naturally adsorbed on the diamond surface. However, the stability of this atmospheric layer, upon which the transfer doping process relies, has been a significant limiting factor in the production of high-power handling and robust operation devices.

One of the materials that can improve the performance and stability of STD in diamond are the metal oxides such as MoO_3 which acts as an alternative electron acceptor medium on the H-diamond surface. In order to validate and understand the physical and the chemical process in such STD, in this work we have combined experimental and simulation studies. The electrical characterisation is done by high temperature Hall measurements. Those experimental results are compared to numerical simulation based on the first principle methods such as Density Functional Theory. Comparing the simulation and experimental results revealed that the electrons are transferred from the diamond to the metal oxides, leading to formation of a sub-surface 2DHG in the diamond. Due to this transfer of electrons to the oxide the hole carrier concentration increases in comparison to the air-exposed H-diamond. Our work shows the potential to improve the stability and performance of hydrogen-terminated diamond electronics devices through incorporation of high electron affinity transition metal oxides.

Plasma Science and Technology Division
Room B131 - Session PS+EM-TuM

Advanced FEOL

Moderator: Alok Ranjan, TEL Technology Center, America, LLC

8:00am **PS+EM-TuM1 Investigation on Plasma Etch Technology Enabling Si/SiGe MOSFET Process Integration***, Yohei Ishii,* Hitachi High Technologies America Inc.*; Y.-J. Lee, W.-F. Wu,* Taiwan Semiconductor Research Institute, Taiwan, Republic of China*; R. Sugano,* Hitachi, Ltd., Japan*; K. Maeda,* Hitachi High Technologies America Inc.*; H. Ishimura,* Hitachi High-Technologies Taiwan Corp., Taiwan, Republic of China*; M. Miura,* Hitachi High Technologies, Japan **INVITED**

Many challenges have emerged due to down-scaling of device structure in order to follow Moore's law. By modifying the transistor structure from planar to Fin-type Field Effect transistors (FinFETs), transistor electro-statics were improved, which led to overcoming short-channel effects. However, the change is no longer sufficient, and the semiconductor industry faces difficulty to further improve the transistor performance. One of the promising candidates for the improvement in sub-10nm process is to utilize Silicon/Silicon-germanium (Si/SiGe) dual channel FinFETs (Si in n-FETs and SiGe in p-FETs). In this case, simultaneous etching of Si and SiGe is required [1]. However, etch rate of SiGe is greater than Si for halogen chemistries commonly used in Si etch. Therefore, it is required to develop selective Si etch over SiGe for etch rate control between these two materials.

In order to maximize electrical performance of SiGe, modifying the SiGe surface composition into Si-rich surface at SiGe/gate-oxide interface is critical to reduce interface state density due to the impact on sub-threshold characteristics [2]. Traditional methods to produce Si-rich surface are epitaxial growth of Si cap over SiGe fin [3] and GeOx-scavenging process [4]. However, thermal budgets of these methods are relatively high, and there are concerns of strain relaxation in SiGe channel and Ge diffusion into Si substrate, both of which deteriorate the FET characteristics. Hence, a low-temperature process to produce Si-rich surface is required.

In this presentation, we will present two phenomena; one is Si-SiGe selective etch control, and the other is SiGe surface composition modification of SiGe into Si-rich surface by low temperature plasma. We will first present a plasma process, which etches Si selective to SiGe for Si-SiGe etching control, and will discuss the etching mechanism of the selective etching. We will then present the composition modification into Si-rich surface by utilizing Si segregation from the low temperature plasma process. This plasma etch technique can solve the etch rate control and surface composition challenges, which can be a promising scheme for realizing well-controlled SiGe finFETs with improved characteristics.

[1]. Y. Ishii et. al., Jpn. J. Appl. Phys. **57**, 06JC04 (2018).

[2]. C. H. Lee et. al., IEDM Tech. Dig., p.31.1.1., 2016

[3]. H. Mertens, et al., VLSI Tech. Dig., p.58, 2014

[4] C.H. Lee, et. al., VLSI Tech. Dig., p. 36, 2016

8:40am **PS+EM-TuM3 Etching of Sub-10 nm Half-pitch High Chi Block Copolymers for Directed Self-Assembly (DSA) Application***, **Maria Gabriela Gusmão Cacho**, P. Pimenta-Barros, K. Benotmane, A. Gharbi, M. Argoud,* CEA-LETI, France*; C. Navarro,* Arkema France, France*; K. Sakavuyi,* Brewer Science Inc.*; R. Tiron, N. Possémé, S. Barnola,* CEA-LETI, France

As the semiconductor industry approaches the smaller technologic nodes such as the sub-10 nm, conventional lithography technologies have reached their limit. Among the different approaches investigated to continue pattern scaling, Directed Self-Assembly (DSA) of Block Copolymers (BCP) is one of the most promising due to its simplicity, low manufacturing cost and capability to design high density cylindrical or line/space patterns. For the last few years, PS-*b*-PMMA has been the most used BCP for this application. However, since the minimum feature size for the PS-*b*-PMMA system is limited to ~13 nm due to its low interaction parameter (also known as "chi"), new systems have been developed to achieve higher resolution by improving its microphase separation strength, thus obtaining the so called "high chi" BCPs.

In this paper, the high chi BCP system investigated is a modified PS-*b*-PMMA that presents a pitch of 18 nm, which will be referred to as "L18". One critical step for its integration is the PMMA removal selectively to the PS. The results obtained with both dry and wet etching of the L18 BCP are presented, highlighting the challenges encountered due to its smaller dimensions.

A wet PMMA removal process based on UV exposure followed by IPA rinse will be presented. An Ar/O_2 dry etch step for the brush layer opening was developed and the transfer of the line/space pattern into the SiO_2 and Si underlayers was demonstrated for the L18 BCP. However, this wet development is expected to cause pattern collapse when the BCP will be guided by chemoepitaxy due to capillary forces.

Therefore a complete PMMA removal by dry etching alone was also investigated. Different etching chemistries based on $CH_3F/Ar/SO_2$, CH_4/N_2 or cyclic CO + CO/H_2 were applied to the modified PS-*b*-PMMA BCPs with a 30 nm pitch and with an 18nm pitch (L18). For the 30 nm-pitch BCP, all three plasma chemistries allow the complete PMMA and brush layer removal by dry etching and the subsequent pattern transfer into the SiO_2 layer. In contrary, for the L18 BCP, the $CH_3F/Ar/SO_2$ plasma does not present enough PS budget for pattern transfer due to its low selectivity and the small thickness of the BCP. For the more passivating chemistries such as CH_4/N_2 and cyclic CO + CO/H_2, which have higher selectivity, we observe the formation of bridges that prevent complete pattern transfer. We used *ex-situ* X-ray Photoelectron Spectroscopy (XPS) to investigate the origin of these bridges and to understand the etching mechanisms present.

9:00am **PS+EM-TuM4 Mechanism of Highly Selective SiCN Etchings Using NF_3/Ar-based Gases***, **Miyako Matsui**,* Hitachi Ltd., Japan*; K. Kuwahara,* Hitachi High-Technologies Corp., Japan

Highly selective etchings over various other materials are increasingly required to achieve self-aligned processes, which provide higher density devices without shrinkage of the pattern dimensions in three-dimensional devices, such as fin-based field-effect transistors. In a self-aligned process, SiCN etching is required to achieve high selectivity to both SiO_2 and Si_3N_4. However, it had been difficult to achieve high selectivities to both SiO_2 and Si_3N_4 using fluorocarbon gas chemistries. For example, selectivity to SiO_2 increased using a hydrofluorocarbon plasma, while selectivity to Si_3N_4 decreased. So, it is important to investigate gas chemistries to simultaneously control selectivities to various materials.

In this study, mechanisms for highly selective SiCN etchings with microwave ECR plasma using NF_3/Ar-based gases were investigated over various materials. The rate of SiCN etching using NF_3/Ar plasma was higher than that of other materials, which were TiN, poly-Si, SiO_2, and Si_3N_4. The SiCN was etched with NF_3/Ar plasma, which formed SiF_x and FCN. On the other hand, other materials were etched with low rates. To achieve higher selectivities, the effects of adding gases to NF_3/Ar plasma on various materials to inhibit etching were analyzed by X-ray photoelectron spectroscopy (XPS).

Firstly, a highly selective SiCN etching over poly-Si was achieved by adding O_2 to NF_3/Ar plasma. This was because poly-Si etching was inhibited by the formation of a 1.0 nm-thick oxidized layer, which protected the poly-Si surface from the etching reaction with F radicals. The SiCN etch rate also decreased when the poly-Si etching was stopped. However, C atoms

contained in the SiCN layer reacted with O radicals and controlled oxidization of the SiCN surface.

Next, highly selective SiCN etchings over SiO_2 and Si_3N_4 were achieved by using a NF_3/Ar-based plasma by which deposited layers were formed on the surfaces. The deposited layers formed on the SiO_2 and Si_3N_4 protected the surfaces from being etched by reacting with F radicals. On the other hand, the deposited layer was thought to be more difficult to be formed on the SiCN.

Lastly, highly selective etching over TiN was achieved by using H_2-added plasma. XPS result showed that a thin protective layer containing TiF_x and ammonium fluoride, which is decomposed over 673K, had been formed on the TiN surface. The protective layer formed on the TiN surface was very effective at protecting the TiN from being etched by F radicals.

In conclusion, we achieved extremely highly selective SiCN etchings over various materials by forming protective layers, which were formed on non-etched materials by adding gases to NF_3/Ar plasma.

9:20am **PS+EM-TuM5 Impact of Plasma Process on Source/Drain Epitaxy Film**, ***Yun Han**, B. Messer, M. Sapel, H. Kim, Y. Shi, M. Wang, Y. Trickett, K. Maekawa,* TEL Technology Center, America, LLC*; K. Taniguchi, S. Morikita,* Tokyo Electron Miyagi Ltd., Japan*; A. Metz, P. Biolsi,* TEL Technology Center, America, LLC

Middle-of-Line (MOL) contact open by plasma etching is a very critical step in logic IC fabrication. Source/Drain Epitaxy (S/D Epi) film as a key element in device transistors controls device performance in various aspects. S/D Epi film damage induced by plasma etch processes have been one of the challenges in MOL integration. Epi film damage includes surface roughening and oxidation, crystal structure relaxation and elemental doping, all of which could lead to uncontrolled variation and degradation in electrical performance of the devices. In this paper, SiGe (known pMOS S/D material) film damage post varying CCP plasma conditions have been studied by utilizing different characterization techniques including X-ray photoelectron spectroscopy (XPS), Transmission Electron Microscope (TEM) / Energy-dispersive X-ray spectroscopy (EDS), Rutherford backscattering spectrometry (RBS) and Secondary ion mass spectroscopy (SIMS). Various CCP plasma conditions include changes in gas chemistries (N/H/O/C/F/Ar), plasma source/bias power and chamber configurations. Electrical response on short loop device wafers have been collected and correlated with observed physical/chemical changes in S/D Epi film post plasma processes. We also performed molecular dynamics, quantum chemistry and chamber scale simulation to understand the fundamental chemical behavior and characterize the surface/chemical properties between provided plasma and SiGe film at various ion energy and ion/radical flux in an atomic/molecular level. The study provides a comprehensive understanding in plasma damage to S/D Epi film and a fundamental guideline in optimizing plasma processes to achieve ideal contact open etch with minimal damage on source/drain Epi film.

9:40am **PS+EM-TuM6 CCP Dry Clean Process Development Using Quadrupole Mass Spectrometer and Optical Emission Spectroscopy**, ***Harutyun Melikyan**, A.D. Martinez, S.C. Pandey, M. Koltonski, G. Sandhu,* Micron Technology

Dual frequency capacitive coupled plasmas provide flexible control of ion energy distributions, enabling high selectivity for etching of different materials, and flexibility to develop more efficient dry clean processes for higher productivity. It is common for each patterned wafer etch to have pre and post dry clean steps, with and without wafer, respectively. The primary focus of dry etch engineers is to design high etch rate processes, with minimized process time, and without changing the critical dimensions. Additionally, significant gains can be achieved by optimizing the dry clean recipes because they contribute significantly to the raw process time. In some cases, it can take a long time to achieve proper pre and post conditioning of the chamber.

In this work, we show that real-time monitoring techniques can be used to provide insight into the etch process byproducts, enabling intelligent development of the dry clean recipes. Integrating quadrupole mass spectrometry and optical emission spectroscopy with the capacitive coupled plasma reactor, and monitoring in parallel, we were able to identify 99% of the patterned wafer etch byproduct species with high confidence. Knowing the etch byproducts provides a clear path to an optimized dry clean process. We were then able to develop the dry clean recipe with appropriate precursor gases to increase volatile byproducts significantly (e.g. SiF4 at 33%) and minimize non-volatile byproducts (e.g. ammonium salts at <1%), resulting in a 70% reduction of dry clean process time.

11:00am **PS+EM-TuM10 Surface Reaction of Atomic Hydrogen with SiGe Surface Compared with Si Through Ab-initio Calculations**, ***Ryoko Sugano**,* Hitachi, Ltd., Japan*; Y. Ishii, K. Maeda,* Hitachi High Technologies America Inc.*; M. Miura, K. Kuwahara,* Hitachi High Technologies, Japan

Simultaneous etching of Si and SiGe is an indispensable process for high throughput in the fabrication of Si/SiGe dual-channel FinFETs. SiGe etch rate is higher than Si etch rate by typical halogen chemistries used for Si etching [1]. Therefore, to control the etch rate between Si and SiGe, it is necessary to develop the chemistry that gives a higher Si etch rate than SiGe etch rate. Recently Ishii et al. have reported that hydrogen plasma selectively etched Si over SiGe, showing the selective Si removal over Ge [2]. In spite of selective Si etching over Ge, the Si-rich surface was observed after the hydrogen plasma exposure. They have attributed the Si-rich surface to hydrogen-induced Si surface segregation [2].

To understand the mechanism of the experimental phenomena on SiGe film described above, we performed ab-initio calculations that combined geometry optimizations and Nudged Elastic Band calculations. In the hydrogen-terminated SiGe surface system, we assumed the reacted states of SiGe were single dimer, in which three hydrogen atoms adsorbed on one of the dimer atoms (SiH3, GeH3) and a single hydrogen atom adsorbed on another of the dimer atoms. We found that the formation with SiH3 was energetically stable and was easy to desorb with a lower activation energy than that with GeH3. We considered that the selective Si removal over Ge was caused by both the selective formation and selective desorption of SiH3. We also calculated the formation energy of the SiGe surface immediately after selective Si removal, which originated from dimer breaking. It was found that the site exchange between the Ge atom in the first layer and the Si atom in the second layer was energetically favorable when another dimer atom left on the surface was terminated with a hydrogen atom. In conclusion, we confirmed experimental results of both selective Si etching over SiGe and Si surface segregation under the condition of hydrogen plasma by performing ab-initio calculations.

[1] G. S. Oehrlein, et al., Appl. Phys. Lett. 58, 2252 (1991).

[2] Y. Ishii et al., Jpn. J. Appl. Phys. 57, 06JC04 (2018).

11:20am **PS+EM-TuM11 Nanopantography with Reusable Membrane-based Electrostatic Lens Arrays**, ***Ryan Sawadichai**, Y.-M. Chen, P. Basu, V.M. Donnelly, P. Ruchhoeft, D.J. Economou,* University of Houston

Nanopantography is a method for massively parallel writing of nano-sized patterns using an ion beam in combination with a reactive gas. In this process, a broad area, collimated, nearly-monoenergetic ion beam is directed towards an array of micron-scale electrostatic lenses in direct contact with a substrate. By applying an appropriate DC voltage to the lens array with respect to the substrate, the ion beamlet entering each lens converges to a fine spot that can be 100 times smaller than the diameter of each lens. Previously, lenses fabricated directly on the silicon substrate were used to etch 3 nm diameter holes in silicon by exposure to a monoenergetic Ar^+ ion beam and chlorine gas. This work reports on the development of removable and reusable free-standing membrane-based electrostatic lens arrays that are designed to pattern any conducting surface. The lens arrays were fabricated on a silicon wafer coated with PMGI, SU-8, gold, copper, and PMMA. Lens openings were lithographically defined, and an acrylic frame was placed over the array. The lens patterns were etched through the SU-8 and the membrane was released by dissolution of the PMGI layer. The applied voltage used to focus the ion beamlets also served to electrostatically clamp the lens array to a conducting substrate, which was observed as a flattening of the membrane against the substrate surface and an increasing capacitance measured between the lens array and the substrate. An array with lens diameters between 0.8 µm and 1.5 µm and dielectric thickness of 1 µm was used to pattern nanoscale features on a silicon substrate using a 70 eV Ar^+ ion beam and chlorine gas. Ion trajectory simulations were performed to understand the sensitivity of minimum feature size to the variation of lens potential, lens aspect ratio, and lens size. Simulations agreed with the experimentally observed patterns when chromatic and spherical aberrations were considered. With a thinner dielectric and higher lens voltage, it should be possible to print sub 10-nm features in a step and repeat nanopantography process.

Plasma Science and Technology Division
Room B130 - Session PS-TuM

Plasma Diagnostics and Sources I

Moderators: Tetsuya Tatsumi, Sony Semiconductor Solutions Corporation, Geun Young Yeom, Sungkyunkwan University, Republic of Korea

8:00am **PS-TuM1 Optimizing Power Delivery in a Pulsed Inductively Coupled Plasma Using Set-Point Impedance Match and Frequency Tuning**, ***Chenhui Qu***, University of Michigan; *J. Brandon, C. Smith, S.C. Shannon,* North Carolina State University; *D. Coumou, S. White,* MKS Instruments; *M.J. Kushner,* University of Michigan

During pulsed operation of inductively coupled plasmas (ICPs) using radio frequency (RF) power, the resistance of the plasma can change by factors of 10-100 while the reactance can change sign (from negative to positive during an E-H transition). These changes in impedance add to the intrinsic impedance of the reactor. The components in the impedance matching network (IMN) hat interface the reactor to the power supply typically cannot be changed rapidly enough to track the plasma transients and maintain a match. The IMN is then tuned to match at a specified time during the plasma pulse, a process called set-point-matching. With feedback control systems and wideband amplifiers, it is possible to make a real-time adjustment of the frequency of the RF oscillator to provide a real-time impedance matching.

In this work, impedance matching to a pulsed ICP plasma was computationally and experimentally investigated using set-point-matching and frequency tuning. The Hybrid Plasma Equipment Model (HPEM) was used for the computational investigation with results compared to experiments performed on the ICAROS reactor, consisting of a four-turn solenoidal coil powering a cylindrical ICP having a 5 cm radius and 15 cm height. The ICPs were operated in Ar at pressures of 1-50 mTorr. The RF power (frequencies from 10-14 MHz) was pulsed modulated at 10 kHz pulsed power with 50 W amplitude and 50% duty cycle.

Set-point-matching early during the pulsed cycle produces more rapid rise in the plasma density while having high reflective power late in the pulse. Set-point-matching late during the pulsed cycle produces a slow rise in the plasma density while having low reflective power late in the pulse. Frequency tuning is able to functionally match during the entire pulsed cycle. For example, when the IMN was set to match in the early period during the pulse, frequency tuning within a range of ±2 MHz is able to maintain reflected power to be less than 10%, and functionally zero late in the pulse. Combinations of set-point-matching and frequency tuning are able to match pulsed-operation over a wide range of power, pressure, pulse repetition frequency and duty cycle.

* Work supported by Samsung Electronics, National Science Foundation and the DOE Office of Fusion Energy Science.

8:20am **PS-TuM2 Compact Surface Wave Plasma Source**, *G.A. Panici,* ***David Ruzic***, *D. Qerimi, D.E. Barlaz,* University of Illinois at Urbana-Champaign; *B.E. Jurczyk,* Starfire Industries LLC

Surface wave plasmas have been used increasingly in industrial applications due to their high electron densities (10^{11-12} cm^{-3}), high radical densities (10^{13-14} cm^{-3}), and low electron temperatures (1-5 eV). Typical radical creation systems generate radicals at a distance from where they are needed. A compact surface wave plasma source can generate and deliver the radicals at the surface where etching is desired. The source is microwave driven, operating in the hundreds of megahertz. At these frequencies, the wave reflects at the plasma sheath boundary due to the cutoff frequency of electrons once the plasma reaches critical density (typically a microsecond). The power is then largely deposited in the sheath, creating a plasma along the surface. In addition to local radical delivery, they can operate from fractions of millitorr to 10 torr and utilize a variety of antenna geometries (lines, arcs, plates).

A compact surface wave plasma source was characterized over a large range of pressures. The electron densities, electron temperatures and radical densities were measured as a function of distance from the plasma source. Multiple gas species were used to investigate the influence on plasma and radical parameters. These results will be presented.

8:40am **PS-TuM3 Overview of Linear Plasma Sources as Applied to Ribbon ion and Plasma Beam Processing of Scanned Substrates**, ***Peter Kurunczi,*** Applied Materials, Varian Semiconductor Equipment **INVITED**

Ribbon beams of ions and plasmas offer unique capabilities within scanned substrate processing techniques such as ion implantation, physical and chemical surface modification, etching and deposition. This talk will cover an overview of ribbon beam technology used across a range of applications, with examples from processing of silicon, glass, and flexible plastic substrates used within semiconductor, display and roll to roll web industries. Various types of linear plasma sources and methods of ion beam generation will be discussed. Of note are the very different types of plasma ion sources used, from magnetized dc discharges driven by thermionic cathodes to rf generated plasmas. The audience is encouraged to extrapolate to how ribbon beams can be used for their specific material processing needs, for example as applied to this year's symposium theme of "Materials, Technologies and Processes for Energy Transition"

9:20am **PS-TuM5 Online Diagnostics of Non-Thermal Plasma Nanoparticle-Laden Systems by Ion Mobility Spectrometry**, ***Xiaoshuang Chen***, *S. Ghosh, D. Buckley,* University of Minnesota, Minneapolis; *R.M. Sankaran,* Case Western Reserve University; *T. Seto,* Kanazawa University, Japan; *U.R. Kortshagen, C.J. Hogan,* University of Minnesota, Minneapolis

Non-thermal plasmas (NTPs) have been shown to be capable of producing chemically-pure, size-controlled, low polydispersity, crystalline nanoparticles (NPs). Vapor-phase precursors are dissociated in the NTP reactor, typically by high electron energy impact, leading to nucleation and NP growth in the gas phase. A prevailing thought is that the NPs are unipolarly charged negative in the plasma, which mitigates coagulation and promotes surface growth, yielding low polydispersity NPs. In this study, we apply ion mobility spectrometry (IMS) as an online diagnostic to NTPs to address particle charging and coagulation.

In the first part of the study, we present an IMS system developed for low pressure to characterize Si nanocrystals synthesized in a radio-frequency (RF), capacitively-coupled NTP operating at 2 Torr. A uniquely designed low-pressure differential mobility analyzer (LPDMA) coupled with an electrical detector was utilized to measure NP size distributions in real time. Via the Twomey-Markowsi inversion approach, we have demonstrated, for the first time, that DMAs can be utilized to analyze NPs synthesized in low-pressure NTPs. Excellent agreement was found between the size distributions measured and inverted by LPDMA system and inferred from TEM images. Importantly, we found that at the outlet of the NTP flow tube reactor, Si NPs are bipolarly charged with nearly identical size distribution functions for both negatively and positively charged NPs. Furthermore, NPs are modestly aggregated, implying that the decharging of NPs exiting the plasma reactor from highly negative charge states to a bipolar charge distribution likely drives aggregation on the plasma boundary.

In the second part, ion-mobility mass-spectrometry (IM-MS) method was implemented to study the morphology of as-synthesized carbon-coated Ni NPs generated in an atmospheric-pressure DC microplasma. Sequentially, NPs were sampled by a DMA that classifies NPs by their mobilities, and an aerosol particle mass analyzer (APM), which separates NPs by masses. The concentration of size-mass classified NPs was measured by a condensation particle counter (CPC) downstream of the DMA-APM system, yielding two-dimensional (2D) size-mass distribution function. The shape and location of the sampled NPs on the 2D contour plot reveal their morphologies and extent of aggregation. Utilizing fractal theory to describe particle mobility, particle morphologies were described quantitatively. Our results demonstrate that Ni NPs leaving the plasma reactor are aggregated in chain-like, low fractal dimension aggregates, which are also verified by TEM images.

9:40am **PS-TuM6 Experiment-Model Comparisons in Capacitively Coupled Plasmas at Moderate Pressures for Argon, Helium and Nitrogen**, ***David J. Peterson***, North Carolina State University; *T. Koh, T.C. Chua, W. Tian, K. Bera, S. Rauf, P.A. Kraus,* Applied Materials, Inc.; *S.C. Shannon,* North Carolina State University

Discharge parameters including electron density, effective collision frequency, effective electron temperature, voltage & current characteristics and sheath thickness around the probe are measured over different pressures and powers ranging from 0.01-4.0 Torr and 10-100 W in Ar, He and N2 plasmas. Fully floating hairpin resonator probes are used in a parallel plate capacitively coupled radiofrequency (rf) discharge driven at 13.56 MHz with a gap distance of 1 inch. Probe measurements are made in the axial and radial directions. 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 must assume an electron energy distribution function (EEDF). Probe sheath thickness is measured using a time resolved measurement system capable of ~5 ns time resolution. High temporal resolution is utilized to measure rf phase resolved electron density and

effective collision frequency. Measurements indicate the presence of enhanced ionization rates near the powered sheath edge in the collisional regime. Electron density peaks at the discharge center at lower pressures, <100 mTorr, and begins to shift towards the powered electrode at higher pressures due to a measurable DC self bias that is known to occur for geometrically asymmetric discharges. The influence of axial probe spatial resolution and approaches for providing sufficient probe isolation from ground are discussed. Spatial profiles of plasma parameters along with voltage & current characteristics are compared with 2-dimensional fluid plasma simulation results. Detailed model-experiment comparisons play an important role in understanding plasma chemistry mechanisms for these low temperature plasmas at moderately high pressure. All analysis and data acquisition is done with python scripts which are freely available to the public.

11:00am **PS-TuM10 Optical and Mass Spectrometric Measurements of O_2 and NF_3 Dissociation in a Low Frequency, High Density, Remote Plasma***, **Hanyang Li**, Y. Zhou, V.M. Donnelly,* University of Houston*; J. Chiu, X. Chen,* MKS Plasma & Reactive Gas Solutions

Remote plasma sources are widely used in many applications, such as chamber cleaning and flowable chemical vapor deposition (FCVD). Processes using remote plasmas are purely chemical in nature, since there are no ions present. In such processes, it is desirable that the dissociation rate of the feed gases in the plasma source be as high as possible, while recombination rates of reactive species on the way to a downstream chamber should be minimized. Only a few studies have been reported on low frequency, high pressure, very high density remote plasma sources. In this paper we present results on radical densities and gas dissociation fractions for a 400 kHz toroidal transformer-coupled plasma source (MKS Instruments), operating at a power density of 5 – 50 W/cm^3 with feed gases mixtures of O_2 or NF_3 with Ar, and pressures of 0.4 or 2.0 Torr. The radical densities and feed gas dissociation percentages in the plasma were measured by optical emission spectroscopy (OES), combined with Ar actinometry. Plasma products flow into an anodized Al downstream chamber that is probed by vacuum ultraviolet (VUV) absorption spectroscopy and line-of-sight molecular beam mass spectrometry, allowing radical and stable species number densities to be determined in the plasma source as well as in the downstream chamber. The dissociation of O_2 and NF_3 was found to be roughly from 60% to 10% with the rise O_2% in plasma and >95% in the plasma source (via Ar actinometry with O and F) and not very dependent of flow rate. Midway across the downstream chamber, substantial recombination of O to form O_2 (via VUV O_2 absorption) occurred; the O/O_2 ratio was a strongly increasing function of increasing flow rate. At the back wall of the downstream chamber, O has nearly completely recombined to O_2 (mass spectrometry), even at the highest flow rate. NF_3 is completely dissociated and does not reform in the downstream chamber; no NF or NF_2 was detected. F was found to be mostly recombined to for F_2 at the back of the downstream chamber. The F_2, F and N_2 product absolute number densities confirmed the 3:1 F:N mass balance of the NF_3 feed gas. The gas temperature at the back downstream chamber was also measured by mass spectrometry, and was found to be 450K for 95% NF_3/Ar at a flow rate from 200 sccm to 600 sccm and 2.0 Torr.

11:20am **PS-TuM11 A Combined Experimental and Modeling Study of Reactive Vapor-nanoparticle-plasma Interactions in a Dusty Atmospheric-pressure Plasma***, **Nabiel Abuyazid**,* Case Western Reserve University*; X. Chen,* University of Minnesota, Minneapolis*; D. Mariotti, P. Maguire,* University of Ulster, UK*; C.J. Hogan,* University of Minnesota, Minneapolis*; R.M. Sankaran,* Case Western Reserve University

Low-temperature (non-thermal), atmospheric pressure plasmas are characterized by several important fundamental and technological advantages for the gas-phase synthesis of nanoparticle materials. However, the effect of the particles on these plasmas remains poorly understood. It is generally accepted that nanoparticles acquire charge, typically negative, which leads to a reduction in the electron (plasma) density. The degree of reduction is not known and experimental measurements are challenged by several issues. One, plasmas operated at atmospheric pressure are small in size (~1 mm) and probes cannot be easily introduced into the plasma volume. Two, there are strong gradients in the plasma volume as the precursor vapor is dissociated and nanoparticles nucleate and grow, and the effect of particles on the plasma must be decoupled. Three, the material could have other effects on the plasma, for example by undergoing further reactions or by vaporizing after particle formation, that must also be isolated or avoided.

We present a tandem, atmospheric-pressure plasma system that separates a first "reactive" plasma, where the precursor vapor is dissociated leading to particle growth, from a second "dusty" plasma, where the effect of particles on the plasma can be studied. Two non-contact methods, an external electrical conductivity probe (Impedans Octiv Poly) and spectroscopy are applied on the dusty plasma to monitor changes in the electron density. We focused our study on carbon which has a relatively high boiling point and should be chemically stable within the plasma environment. The measurements show that electron densities decrease as expected upon the introduction of the nanoparticles into the second plasma at all powers. For example, at a power of 50 W, the electron density decreased from 4.0×10^{14} cm^{-3} for a pure Ar plasma to 3.6×10^{14} cm^{-3} for a dusty Ar plasma with a total particle concentration of about 4.0×10^6 particles/cm^3. Monte Carlo simulations were carried out in support of experiments and showed that by preferential negative charging, particles in plasmas can reduce bulk electron concentrations. We will also discuss the effect of residual hexane vapor and possible particle evaporation on plasma properties.

Atomic Scale Processing Focus Topic
Room B130 - Session AP+EL+MS+PS+SS+TF-TuA

Advancing Metrology and Characterization to enable Atomic Layer Processing

Moderators: Eric A. Joseph, IBM T.J. Watson Research Center, Jessica Kachian, Intel Corporation

2:20pm **AP+EL+MS+PS+SS+TF-TuA1 In Situ Ellipsometry Characterization Of Atomic Layer Processes: A Review*, James Hilfiker,*** *G.K. Pribil, J. VanDerslice,* J.A. Woollam Co., Inc. **INVITED**

Atomic layer processes such as atomic layer deposition (ALD) and atomic layer etch (ALE) provide monolayer-level thin film deposition or etch. Spectroscopic ellipsometry (SE) is ideally suited for the characterization requirements of such very thin layers. In situ SE provides real-time feedback, which is invaluable for establishing new atomic layer processes. In situ SE characterization has been adopted by many researchers due to its versatility. SE measurements are sensitive to deposition or etch at the (sub)monolayer level. The real-time evolution of film thickness provides details on nucleation periods or delays, the growth or etch rates per cycle, and verifies the self-limiting nature of a process. Multiple experiments can be performed within a single run by modifying the process conditions, allowing quick qualification of deposition temperatures, chemical exposure times, plasma influences, and purge times. In this paper, we will review the areas where in situ SE has been applied to both atomic layer deposition and etch.

We will also discuss the applications of in situ SE that benefit from a broad wavelength range. SE is best known for determining film thickness and optical constants. This characterization can be accomplished for many types of materials – dielectrics, semiconductors, organics, and even metals – provided the layer remains semi-transparent. Other material properties affect the optical constants and can be determined via this relationship. In situ SE has been used to estimate the crystal structure, composition, and even conductivity of thin films. We will discuss the advantages and limitations of in situ SE, which in many ways has proven to be an ideal partner for atomic layer processes.

3:00pm **AP+EL+MS+PS+SS+TF-TuA3 Elucidating the Mechanisms for Atomic Layer Growth through In Situ Studies*, Jeffrey Elam,*** Argonne National Laboratory **INVITED**

Atomic Layer Deposition (ALD) provides exquisite control over film thickness and composition and yields excellent conformality over large areas and within nanostructures. These desirable attributes derive from self-limiting surface chemistry, and can disappear if the self-limitation is removed. Understanding the surface chemical reactions, i.e. the ALD mechanism, can provide insight into the limits of self-limitation allowing better control, successful scale up, and the invention of new processes. In situ measurements are very effective for elucidating ALD growth mechanisms. In this presentation, I will describe our recent investigations into the growth mechanisms of ALD nanocomposite films comprised of conducting (e.g. W, Mo and Re) and insulating (e.g. Al_2O_3, ZrO_2 and TiO_2) components using in situ measurements. These ALD nanocomposites have applications in particle detection, energy storage, and solar power. We have performed extensive in situ studies using quartz crystal microbalance (QCM), quadrupole mass spectrometry (QMS), Fourier transform infrared (FTIR) absorption spectroscopy, and current-voltage measurements. These measurements reveal unusual ALD chemistry occurring upon transitioning between the ALD processes for the two components. This results in unique reaction products that affect the properties of the films in beneficial ways. The knowledge gained from our in situ studies of the ALD nanocomposite films has helped us to solve problems encountered when we scaled up the ALD processes to large area substrates.

4:20pm **AP+EL+MS+PS+SS+TF-TuA7 Surface, Interface, or Film: A Discussion of the Metrology of ALD Materials in Semiconductor Applications*, G. Andrew Antonelli,*** *N. Keller,* Nanometrics **INVITED**

Atomic layer deposition, etching, and interface engineering are enabling technologies for semiconductor manufacturing. These processes have led to an explosion in the use of laboratory techniques such as transmission electron microscopy and the need to bring such instruments closer to or into the fab itself. However, there remains a need for in-line, non-destructive, non-contact metrology capable of quickly characterizing and monitoring these extremely thin films on test structures, on product, or in device as these data are the only meaningful method for monitoring of ultimate device performance. Indeed, in cases such as the use of selective deposition or etching, no test vehicle other than the ultimate product may be relevant. A variety of measurement techniques with a focus on x-ray and optical probes as applied to this class of problems will be reviewed. Examples will be provided on relevant logic such as the Gat-All-Around FET and memory devices such as 3D NAND.

5:00pm **AP+EL+MS+PS+SS+TF-TuA9 In Line and Ex Situ Metrology and Characterization to Enable Area Selective Deposition*, Christophe Vallee,*** *M. Bonvalot, B. Pelissier, J-H. Tortai, S. David, S. belahcen, V. Pesce, M. Jaffal, A. Bsiesy,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; R. Gassilloud, N. Posseme,* CEA-LETI, France*; T. Grehl, P. Bruner,* IONTOF GmbH, Germany*; A. Uedono,* University of Tsukuba, Japan

Innovation in materials, architectures (3D), gap filling technologies, lithography and etch processes are mandatory at every node of CMOS or memory devices. These challenging integration issues can be facilitated by the use of an integration scheme currently being intensively investigated known as area selective deposition (ASD). Criteria for an adequate area selective deposition process are: growth only on specific regions, high throughput compatible with industrial demands, no so-called mushroom profiles into adjacent features as well as no nuclei defectivity on undesired sites. Several routes can be developed to achieve an ASD process with ALD. The one discussed here concerns the deposition/etch approach which takes benefit from an *in situ* etching step inserted in a standard ALD cycle [1]. By incorporation of anisotropic or isotropic etching steps in the ALD process, “surface” selective deposition, as well as topographically selective deposition (TSD) have been obtained [2, 3]. The major current shortcoming of this approach lies in the deep insight which is required regarding elementary atomic-scale reaction mechanisms. Indeed, in the case of an ALD/ALE Area Selective Deposition process, a highly precise control of etching and its selectivity at the atomic scale is needed. Controlling the nature and density of defects induced by etching or passivation steps and understanding their impact on the physical and electrical properties of selectively deposited films are of course also required. Moreover, in order to optimize these processes, an accurate understanding of the underlying reasons why passivation after a low number of ALD cycles, is no more effective. Thus, *in situ* as well as *ex situ* monitoring and metrology are mandatory.

In this presentation, we will discuss how to optimize and understand atomic-scale reaction mechanisms in an ALD/ALE ASD process using combined *in situ* or *ex situ* measurements, such as ellipsometry, XPS, XRR, LEIS, FIB-STEM, and positron annihilation. We will show that when crosslinked, these technics are very effective to perform atomic scale metrology and characterization. As an example, we will discuss F atom localization and density in selectively deposited oxides thanks to a F-based ALE chemistry incorporated in the ALD process. In the case of a topographically selective deposition (TSD) process attempts will be presented to understand ion/surface interactions when low energetic ions are extracted from the plasma of the PEALD reactor both during deposition and plasma-ALE steps.

[1] R. Vallat et al, JVSTA **35** (2017) 01B104

[2] R. Vallat et al, JVSTA **37** (2019) 020918

[3] A. Chacker et al, APL **114** (2019)

5:20pm **AP+EL+MS+PS+SS+TF-TuA10 Recent Progress in Thin Film Conformality Analysis with Microscopic Lateral High-aspect-ratio Test Structures*, Riikka Puurunen,*** Aalto University, Finland **INVITED**

Conformal thin films which cover complex 3D shapes with a film of uniform properties (thickness, composition, etc.) are increasingly demanded applications such as semiconductor devices, microelectromechanical systems, energy conversion/storage and catalysis. Atomic layer deposition (ALD) and its counterpart atomic layer etching (ALE) [together known as atomic layer processing (ALP)], are increasing in usage largely thanks to their known conformal character.

A question that needs to be asked in the R&D of 3D applications using conformal ALD/ALE processes is: how conformal is conformal; is the conformality sufficient to meet the specs? In semicon industry, vertical vias and cross-sectional transmission electron microscopy (TEM) are standardly used for conformality analysis. Recently, microscopic lateral high-aspect-ratio (LHAR) test structures have been developed to improve the conformality analytics capabilities. LHAR structures e.g. enable detailed conformality analysis at arbitrarily high aspect ratios (e.g., >5000:1), where no film can coat the 3D structure fully, thereby exposing the saturation

profile characteristic for the process. This, in turn enables the kinetic analysis of the process and e.g. extraction of the sticking coefficients related to the growth reactions.

This invited talk will address recent progress related to the fabrication and the use of microscopic LHAR conformality test structures. After the breakthrough with the first prototypes (PillarHall LHAR1; Gao et al. 2015, Mattinen et al. 2016; reviewed in Cremers et al., 2019), third and fourth generation prototypes have been developed (PillarHall LHAR3 and LHAR4). This work will review the conformality analysis progress enabled by the microscopic LHAR structures and discuss the benefits and challenges of this approach. Recent published progress includes the conformality modelling by Ylilammi et al. (2018) and experimental extraction of sticking coefficient by Arts et al. (2019). In addition, several other ongoing conformality analysis cases will be presented.

References

Arts, Vandalon, Puurunen, Utriainen, Gao, Kessels, Knoops, J. Vac. Sci. Technol. A 37, 030908 (2019); https://doi.org/10.1116/1.5093620

Cremers, Puurunen, Dendooven, Appl. Phys. Rev. 6, 021302 (2019); https://doi.org/10.1063/1.5060967

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Ylilammi, Ylivaara, Puurunen, J. Appl. Phys. 123, 205301 (2018); https://doi.org/10.1063/1.5028178

6:00pm **AP+EL+MS+PS+SS+TF-TuA12 *In operando*XPS Study on Atomic Layer Etching of Fe and Co Using $Cl_2$and Acetylacetone or Hexafluoroacetylacetone***, **Zijian Wang**, O. Melton, D. Angel, B. Yuan, R.L. Opila,* University of Delaware

Etching of transition metals is one of the major challenges in magnetoresistive random-access memory (MRAM) device fabrication. In this work, atomic layer etching of iron and cobalt surfaces with halogen and an organic molecule was studied. We successfully performed etching of Fe and Co thin films via forming volatile metal complexes at low temperature with cyclic sequential reactions of Cl_2 and acetylacetone (acac) or hexafluoroacetylacetone (hfac) . The etching reaction mechanism of acac and hfac reacting with Clorine-modified Fe and Co surfaces was investigated: the surface was first activated with Cl_2 gas, and subsequently, the top layer of chlorinated metal was removed by reaction with a diketone (acac/hfac). The extent of Cl_2 reaction determines the etching rate of the metal. At substrate temperatures lower than 135°C, acac could remove the chlorinated Fe metal layer from Fe surfaces, but not chlorinated Co from Co surfaces. *In-operando* x-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) simulation shows that the reaction of acac or hfac with Chlorinated Fe or Co surfaces is likely following a complex reaction pathway instead of simple diketone substitution for the metal chloride. Diketone decomposition may play an important role in the etching process.

Plasma Science and Technology Division
Room B131 - Session PS+EM-TuA

Advanced BEOL/Interconnect Etching and Advanced Memory and Patterning

Moderators: Hisataka Hayashi, Kioxia Corporation, Japan, Kenji Maeda, Hitachi High Technologies America Inc.

2:20pm **PS+EM-TuA1 BEOL Etch Challenges and Solutions for Advanced Process Nodes***, **Angélique Raley**, K. Lutker-Lee, X. Sun, Y.-T. Lu, Q. Lou, N. Joy, M. Edley,* TEL Technology Center, America, LLC*; K. Taniguchi, M. Honda,* TEL Miyagi Limited, Japan*; P.E. Biolsi,* TEL Technology Center, America, LLC **INVITED**

As logic nodes continue to scale below 7 nm, the back-end-of-line (BEOL) critical pitch has moved to sub-40 nm and is forecasted to scale down to 14 nm according to the latest International Roadmap for Devices and System (IRDS). This aggressive scaling has led to an industry wide effort in terms of materials research to manage interconnect resistance, patterning innovations to control for process variation impact and an increased focus on self-limited or highly selective processes.

In addition to the patterning and integration complexities that arise with scaling, pitch reduction has a direct impact on the plasma etch-processing window. Conventional continuous wave processes can no longer achieve stringent aspect ratio dependent etching (ARDE), selectivity and profile control requirements and have gradually given way to pulsed plasma processes, decoupled process sequence plasmas or remote plasmas to widen the process space.

In this talk, we will give an overview of plasma etching challenges and solutions for the BEOL in terms of patterning integration, dielectric etch and new materials introduction.

3:00pm **PS+EM-TuA3 Enabling Fully Aligned Via for Advanced BEOL Nodes Scaling -Etch and Film Co-optimization***, **Xinghua Sun**, A. Raley,* TEL Technology Center, America, LLC*; J. Lee, J.C. Arnold,* IBM Research Division, Albany, NY*; K. Taniguchi,* TEL Miyagi Limited, Japan*; M. Edley, K. Lutker-Lee,* TEL Technology Center, America, LLC*; D. O'Meara,* Tokyo Electron America, Inc.*; K. Tapily, Y.-T. Lu, P.E. Biolsi,* TEL Technology Center, America, LLC

Aggressive metal pitch scaling of back end of line (BEOL) interconnect for future nodes leads to increased sensitivity to via overlay and critical dimension (CD) errors, resulting in yield loss. Spacing between top and bottom metal layers in via chain macros are reaching the limits of current materials, such that device reliability may become compromised due to metal shorting or dielectric breakdown. The technique of 1-D self-aligned via (SAV) constrained by top metal hard mask (MHM) is widely used to control one direction of via CD. 2-D fully aligned via (FAV) was recently introduced to mitigate the drawbacks of SAV at via bottom. In FAV, vias are constrained with spacers resulting from recessed metal in the orthogonal direction to the MHM, thereby increasing the margin of error allowed due to CD variations and overlay shifts. However, one of the biggest challenges in successfully integration of FAV in the BEOL is maintaining the integrity of these spacers during via etch. Etch selectivity, landing on conformably deposited Nblok based cap layers, is far from sufficient to maintain good self-confinement that demonstrates adequate FAV behavior. High selectivity etch stop layers (ESL) along with compatible etches that promote soft landing on these films are required.

In this presentation, we demonstrate that etch and film can collaboratively work to make FAV a competitive solution for sub-7nm nodes. Different ESL materials and film properties are investigated in conjunction with unique via and trench etch processes to achieve optimized FAV corner shape. This work shows a multifaceted approach to successful implementation of FAV as a valuable scaling booster for advanced BEOL nodes.

3:20pm **PS+EM-TuA4 Non-selective Silicon Oxide and Nitride Etch in Oxygen/Nitrogen-containing Fluorocarbon Plasmas***, **Yu-Hao Tsai**, D. Zhang, Y. Han, J. Baillargeon, Y. Shi, H. Kim, M. Wang,* TEL Technology Center, America, LLC*; T. Yokoyama, M. Iwata, Y. Kihara, M. Honda, W. Sakamoto,* Tokyo Electron Miyagi Ltd., Japan*; A. Mosden, A. Metz, P.E. Biolsi,* TEL Technology Center, America, LLC

Performing an all-in-one etch process for 3D-NAND fabrication requires comparable and high etch rates (E/R) for SiO_2 and Si_3N_4; the goal remains challenging. As the discrepancy of E/R largely results from the different nature of materials, surface modifications of SiO_2 and Si_3N_4 to achieve comparable composition during etch can improve the desired non-selectivity. In the presented work, we study the conversion of SiO_2 [*Submitted*] and Si_3N_4 [*J. Micro. Manuf.***1**, 20180102 (2018)] to oxynitride (SiO_xN_y) via the nitridation and oxidation-etch reactions, respectively. We computationally identify the etching mechanism of SiO_2/Si_3N_4 in the N/O-containing fluorocarbon plasmas using both quantum chemistry (QC) and molecule dynamics (MD) simulations; the surface conversion to SiO_xN_y is predicted. The results are further validated by the plasma etching of blanket SiO_2 and Si_3N_4 films in a Capacitively Coupled Plasma (CCP) chamber; both E/R trends and surface analysis on validation of oxinitride and/or nitrioxide (SiO_xN_y) formation using methods such as XPS, EDS etc. are discussed. We detail the etch reaction pathway, in which the elimination of O/N atom forming nitric oxide (NO) species is predicted. Along with that, the synergy of having F species in the process is justified. Finally, we discuss the impact of fluorocarbon to N/O ratio on the preference of either high E/R or active SiO_xN_y formation. The research builds a foundation for future development work on pursuing robust all-in-one non-selective SiO_2/Si_3N_4 etch processes.

4:20pm **PS+EM-TuA7 Challenges in High-aspect-ratio Hole Etching for 3D Flash Memory***, **Mitsuhiro Omura**, J. Hashimoto, T. Adachi, Y. Kondo, M. Ishikawa, J. Abe, I. Sakai, H. Hayashi,* Kioxia Corporation, Japan **INVITED**

Memory devices with higher bit density are required for effective use of big data in the internet of things era, and 3D memory architecture is required. 3D flash memory encompasses numerous pillars that punch through

control gate plates, and cells are arranged along the pillars [1]. We refer to each pillar as a memory hole. Memory holes are fabricated by dry etching of stacked films, which are generally constructed of dozens to several hundred pairs of SiO2/Si or SiO2/Si3N4 films. Therefore, the aspect ratio of a memory hole reaches several tens. Moreover, the critical dimension and profile of a memory hole must be strictly controlled because these features at each control gate plate directly affect the characteristics of memory cell. Therefore, the key technology of 3D flash memory is a high aspect ratio (HAR) hole etching process. However, the dry etching process of HAR holes has a variety of profile issues, including bowing, shape distortion, twisting of the hole profile, and striation.

In this study, sidewall striation formation in a HAR hole was investigated. In spite of the smooth morphology of the mask, sidewall striation was observed on dielectric films. Results from the carbon mask sample treated with several gas plasmas implies that ion irradiation can increase the degree of striation on the carbon mask, and striation tends to be suppressed by deposition of a fluorocarbon film from fluorocarbon radicals. An ion beam experiment with a simulated hole sidewall using blanket films shows that striation tends to form on the fluorocarbon film rather than on SiO2 and Si3N4 films. In connection with this result, the shallower region with striation had thicker fluorocarbon film than the deeper region with smooth sidewall. Therefore, the possible of sidewall striation formation mechanism is as follows. When the etching depth of the HAR holes reaches a certain depth, striation forms on the deposited fluorocarbon film and is transferred to the dielectric films laterally as the hole diameter increases. The region with striation depends on the aspect ratio, defined as the depth divided by the neck width of the carbon mask. Consequently, as etching progresses, the mask thickness decreases and striation forms in a deeper region, depending on the aspect ratio.

References

[1] H. Tanaka et al., Symposium on VLSI Technical Digest, 14 (2007).

5:00pm **PS+EM-TuA9 Plasma Processing of Phase Change Materials*,* *Ernest Chen,*** *N.D. Altieri,* University of California, Los Angeles*; C.M. Neumann, S.W. Fong, H.-S.P. Wong,* Stanford University*; M. Shen, T.B. Lill,* Lam Research Corporation*; J.P. Chang,* University of California, Los Angeles

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. Ternary chalcogenide glasses consisting of germanium, antimony, and tellurium are widely used in PCRAM applications, and Ge_2Sb-$_2Te_5$ (GST-225) will be the focus of this study.

Understanding the effects of plasma processing on the phase change material (PCM) utilized in PCRAM is crucial to ensuring proper device performance. The studies presented in this talk utilize a custom-built integrated system equipped with ion beam processing, downstream plasma processing, quadrupole mass spectrometry, optical emission spectroscopy, and x-ray photoelectron spectroscopy capabilities. The samples are prepared by sputtering from a stoichiometric GST-225 target. Prior studies have examined the behavior of GST-225 when exposed to different components of ambient exposure (N_2, O_2, and H_2O) as well as H_2 and CH_4 discharges and identified H_2 and CH_4 as capable GST etchants.

It is known that ambient exposure will cause a GST-225 layer to be oxidized in the first several nanometers, and this oxidized layer has different properties from the bulk of the GST-225 film and may also behave differently from the bulk material when exposed to plasma processing. Initial studies with *ex-situ-* XPS analysis indicate that H_2 can etch GST-225 with approximately 5% change in composition (5% increase in Ge, 5% decrease in Sb, approximately 0% change in Te) and a significant change in the ratio of 0+ to X+ (non-oxidized to oxidized) bonding states between the oxidized surface and the etched surface. In order to distinguish the effects of plasma processing on the oxidized layer and the bulk material, a custom-built downstream plasma processing chamber integrated with an XPS chamber is used. This system allows for the study of the surface states of GST-225 post-processing without any inadvertent effects from ambient conditions that may complicate *ex-situ* XPS analysis.

5:20pm **PS+EM-TuA10 Meeting the Challenges in Patterning Phase Change Material for Next Generation Memory Devices*,* *Meihua Shen,*** *L. Thorsten, J. Hoang, S. Chiou, D. Qian, A. Routzahn, J.K. Chen, A. Dulkin, J. Sims, A. McKerrow, R. Dylewicz,* Lam Research Corporation **INVITED**

Phase change materials (PCM) have emerged as the leading candidate for next generation non-volatile memory device with unique characteristics that significant differ from conventional DRAM and NAND flash memory. Recently, 3-D Cross point PCRAM, for example, has transitioned into high volume production, demonstrating a non-volatile memory product exhibiting faster speed, low voltage operation and high density.

Phase change materials are typically chalcogenide alloys containing elements such as Ge, Sb, Se, Te with various dopants. The materials exhibited phase change between amorphous insulating state and the crystalline conductive state under thermal/electric heating. To ensure electric device performance, it is critically important to maintaining the PCM elemental composition and structure integrity during patterning. The challenges of patterning PCM come from the soft nature of the material and the damages that can easily occur during plasma dry etch, ambient air exposure, wet clean and encapsulation process. To meet the challenges, we developed an integrated system combining dry etch, wet clean and ALD encapsulation modules together. In this paper, we will present the comprehensive studies on each module as well as the interactions of the modules in successful patterning of the phase change materials. The discussions will be focused key learnings on how to maintain the feature fidelity and the integrity of the materials during etch and encapsulation.

6:00pm **PS+EM-TuA12 Utilizing Photosensitive Polymers to Estimate UV Radiation Exposures in Different Plasma Chamber Configurations*,* *Luxherta Buzi,*** *M.P. Sagianis, S.U. Engelmann,* IBM T.J. Watson Research Center

Monitoring vacuum ultraviolet (UV/VUV) emission in plasma systems is challenging as it requires specialized diagnostic systems or sensors to be compatible with reactive ion etch (RIE) tooling. This study is mapping different reactor configurations with various levels of UV emission and its effect on a known set of polymers.

Photon-induced modifications on polymers can help decouple ion and photon effects on materials therefore, the impact of inductively coupled and microwave plasma configurations on etch rates and chemical properties of photoresists were investigated. Poly(methyl methacrylate) and Poly(4-hydroxystyrene)-based photoresists were deposited on Si wafers and exposed to argon (Ar) and nitrogen (N_2) plasmas which generate different levels of UV irradiation. X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared (FTIR) were used to analyze the polymer composition and molecular structure and the surface roughness was analyzed with an atomic force microscope (AFM).

FTIR and XPS confirmed that N_2 plasma effects on chemical modifications were more pronounced on the Poly(methyl methacrylate). Roughness and etch rate was significantly higher for Poly(methyl methacrylate) compared to Poly(4-hydroxystyrene)-based photoresists. Detailed elemental and molecular structure analysis of polymers showed relatively higher damage caused from the inductively coupled plasma, which is ultimately correlated to a higher UV emission.

Thin Films Division
Room A124-125 - Session TF+PS-TuA
Epitaxial Thin Films

Moderator: Robert Grubbs, Micron Technology

2:40pm **TF+PS-TuA2 Van der Waals Layer Promoted Heteroepitaxy in Sputter-deposited Transition-metal Carbide and Sulfide Thin Films*,* *Koichi Tanaka*[1]*,*** *P. Arias, M.E. Liao, Y. Wang, H. Zaid, A. Aleman,* University of California, Los Angeles*; K. Hojo,* Nagoya University, Japan*; A. Deshpande, M.S. Goorsky, S. Kodambaka,* University of California, Los Angeles

Over the past decade, two-dimensional (2D) layered materials such as graphene, MoS_2, etc., have attracted considerable attention for a variety of applications, primarily in nanoelectronics and optoelectronics. An exciting and relatively little explored application of these van der Waals (vdW) layered materials is their use as templates for crystal growth. In the recent years, vdW layers present at the substrate-film interface have been shown to promote 'remote epitaxy', by relaying the epitaxial registry between the film and the substrate.

[1] **National Student Award Finalist**

Here, we demonstrate that the crystallinity of sputter-deposited thin films can be significantly improved using vdW layered materials as buffer layers on growth substrates. Using 2D hexagonal boron nitride (hBN, a = 0.250 nm and c = 0.667 nm) as the buffer layer, we grow hexagonal-MoS_2 (a = 0.315 nm and c = 1.23 nm), trigonal-structured Ta_2C (a = 0.310 nm and c = 0.494 nm), and NaCl-structured TaC (a = 0.446 nm) of desired thickness on Al_2O_3(0001) substrates via ultra-high vacuum direct current magnetron sputtering of Mo and TaC targets respectively, in Ar/C_2H_4 and Ar/H_2S gas mixtures. hBN layers are deposited in the same system via pyrolytic cracking of borazine (~600 L) onto the substrates at prior to the growth of the thin films. The as-deposited films are characterized using a combination of *in situ* using Auger electron spectroscopy and low-energy electron diffraction and *ex situ* X-ray diffraction (XRD), X-ray photoelectron and Raman spectroscopies, and transmission electron microscopy (TEM) based techniques.

We find notable differences in the layers deposited on hBN-covered Al_2O_3(0001) compared to those grown on bare substrates: significantly stronger 0002 (or 111 in case of TaC) reflection intensities and observation of Laue oscillations in ω-2θ XRD scans and higher intensity of MoS_2 characteristic peaks in Raman spectrum. Furthermore, we show that inserting hBN layers at regular intervals results in highly-0002-oriented growth and suppression of polycrystallinity in thicker Ta_2C films. Our results indicate that hBN layers enhance the crystallinity, irrespective of the crystal structure, of sputter-deposited thin films.

3:00pm **TF+PS-TuA3 Molecular Beam Epitaxy Applied to Tensile-Strained Quantum Dots for Quantum Optics and Band-Structure Engineering*, Paul Simmonds,*** Boise State University **INVITED**

Since the early 1990s, solid-state self-assembled quantum dots (QDs) have been the subject of intensive research for devices and technologies ranging from high-stability lasers, to intermediate band solar cells. Driven by compressive strain, semiconductor QDs form spontaneously on the (001) surfaces of both III-V and group IV materials during growth by molecular beam epitaxy (MBE). But several years ago, I became interested in the question of why QD self-assembly seemed to be limited to materials with this specific combination of compressive strain, and a (001) surface orientation. For example, why could we not grow QDs under *tensile* rather than compressive strain or on non-(001) surfaces, especially since QDs with these characteristics are predicted to be highly desirable for certain applications. The low fine-structure splitting of (111) QDs should make them ideal entangled photon sources; tensile-strained QDs would have dramatically reduced semiconductor band gaps, with implications for infrared optoelectronics and nanoscale band structure engineering.

The first step towards answering this question was to understand how the competition between plastic and elastic strain relief mechanisms made it enormously challenging to synthesize non-(001) or tensile-strained QDs without the formation of crystallographic defects. The outcome of this analysis was the discovery of a robust new approach to QD self-assembly based on MBE that overcomes these difficulties, and enables the reliable, controllable growth of defect-free, tensile-strained QDs on (111) and (110) surfaces.

I will describe the model upon which tensile-strained QD self-assembly is founded, and then discuss the application of this novel growth mode to several different material systems. I will present data confirming that the (111)-oriented QDs we can now grow do indeed show promise as entangled photon sources. I will highlight the possibilities for band structure engineering that are now available with tensile-strained QDs, using the example of transforming germanium into a direct band gap semiconductor.

In summary, I hope to demonstrate that tensile-strained self-assembly represents a powerful new tool for heterogeneous materials integration, and nanomaterial development.

5:00pm **TF+PS-TuA9 Low-temperature Homoepitaxial Growth of N-type Superlattices for Ultrastable, Ultrafast X-Ray and Charged Particle Detectors*, April Jewell,*** Jet Propulsion Laboratory, California Institute of Technology*; M.E. Hoenk,* Jet Propulsion Laboratory*; Q. Looker, M.O. Sanchez, B.D. Tierney,* Sandia National Laboratories*; A.G. Carver,* Jet Propulsion Laboratory*; S. Nikzad,* Jet Propulsion Laboratory, California Institute of Technology

We present a low-temperature process for the homoepitaxial growth of antimony superlattices in silicon. The all low temperature superlattice doping process is compatible as a post-fabrication step for device passivation. We have used low-temperature molecular beam epitaxy (MBE) to embed atomically thin (2D), highly concentrated layers of dopant atoms within nanometers of the surface. This process allows for dopant densities on the order of 10^{13}-10^{14} cm^{-2} (10^{20}-10^{21} cm^{-3}); higher than can be achieved with three-dimensional (3D) doping techniques. This effort builds on our prior work with n-type delta doping; we have optimized our growth processes to achieve delta layers with sharp dopant profiles. By transitioning from a standard effusion cell to a valved cracker cell for antimony evaporation, we have achieved carrier densities approaching 10^{21} cm^{-3} with peak distribution at ~10 Å FWHM for single delta layers. We will discuss details related to growth optimization, and show results from in situ monitoring by electron diffraction. We will also report on elemental and electrical characterization of our films.

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.

5:20pm **TF+PS-TuA10 Epitaxial Growth of Ultrathin Molybedenum Nitrides on Ru(0001) and Ag(100)*, Asim Khaniya,*** *M. Sajid, A. Kara, W.E. Kaden,* University of Central Florida

Molybdenum-nitrides are known to possess interesting mechanical, electronic, and catalytic properties. For example, (i) hexagonal δ-MoN exhibits mechanical elasticity and hardness values comparable to cubic BN and diamond, (ii) both hexaganol and cubic phases of molybdeumn nitrides are known to be superconducting, and (iii) mixed-phase structures have been shown to outperform commercial hydrotreatment catalysts for selective nitrogen removal from heterocyclic organic feedstocks. To better understand these properties, many groups have worked to create improved recipes to grow different phase-pure crystallographic phases of the material. To-date, the most successful procedures have leveraged epitaxy to improve long-range bulk order, but have lacked the well-defined, planar terminations suitable for controlled surface-science investigations. To establish such samples, our group has opted to use low energy nitrogen ions in tandem with molybdenum physical vapor deposition to grow and characterize molybdenum-nitride films on Ru(0001) and Ag(100) supports, which have been chosen to template the growth of hexaganol and cubic phases of the nitride. At the time of this abstract submission, we have succeeded in the growth of a δ-MoN-like film that appears to grow layer-by-layer and in registry with the Ru(0001) support, and are now in the early stages of repeating the process to create γ-Mo_2N on Ag via an analogous process. This talk will focus on the interesting aspects of these materials (particularly those relevant to catalysis), our approach to film preparation, and a thorough analysis of the physical properties of the resultant films and growth modes via: XPS, LEED, He^+ Ion Scattering Spectroscopy, STM, and DFT.

5:40pm **TF+PS-TuA11 Using Time and Temperature of the Purge Step to Control Crystallinity, Phase Assemblage, and Epitaxy in Atomic Layer Deposited (ALD) Thin Films*, Mark Losego,*** *B.D. Piercy, R.J. Petrie,* Georgia Institute of Technology

The purge step between precursor and co-reactant doses in an atomic layer deposition (ALD) process is often viewed as a process liability. The goal for most manufacturing processes is to make this purge step as short as possible without disrupting the quintessential self-limited growth of ALD. In our lab, we have instead viewed this purge step as a potential opportunity to influence the crystallinity and phase assemblage of our materials. In actuality, each of these purge steps are an opportunity to allow surface diffusion to rapidly reform the film's microstructure before the next layer is deposited. Throughout the literature are interesting, but often conflicting reports of how ALD films crystallize with temperature and thickness. In our recent work, we have asked some simple questions, like how does the onset of such crystallinity change with purge time? We have found, for example, that the onset of anatase formation in the $TiCl_4$-H_2O ALD system can be reduced by more than 40 °C by simply extending the purge time between each cycle. While potentially time intensive, these results have implications for depositing crystalline materials on temperature-sensitive substrates, like polymers. We also find that often an initial seeding of the crystallinity can lead to accelerated growth of crystalline phases with subsequent cycles. In a second paradigm to be discussed, we have introduced a high-temperature pulsed heating source to an ALD system to intentionally crystallize materials and drive epitaxial growth. As proof-of-concept, we have studied epitaxial growth of ZnO on c-plane sapphire using a diethylzinc (DEZ) / water chemistry. DEZ is known to decompose above

about 180˚C, and the DEZ-H_2O system cannot be grown epitaxially on c-sapphire with traditional thermal ALD approaches. Here, we show that heating pulses up to 900˚C can be used to drive epitaxy. Interestingly, we find that a template layer of only 20 pulsed heating ALD cycles is sufficient to template ZnO epitaxy with subsequent low temperature ALD growth (180 °C) to film thicknesses of up to 100 nm.

6:00pm **TF+PS-TuA12 The Role of Template Layers in Heteroepitaxial ALD Growth of Crystalline La_2O_3 on GaN(0001)***, **Pei-Yu Chen**, T. Hadamek,* University of Texas at Austin*; S. Kwon,* University of Texas at Dallas*; F. Al-Quaiti, A. Posadas,* University of Texas at Austin*; M.J. Kim,* University of Texas at Dallas*; A.A. Demkov, J.G. Ekerdt,* University of Texas at Austin

The high switching frequency, operating temperatures and voltages make GaN the material of choice for higher power applications and instrumental to reducing power consumption. In many of these applications, there is a need for a high quality gate dielectric. Lanthanum sesquioxide, La_2O_3, is one of the promising gate insulator candidates. In this work, we compare La_2O_3 thin films grown by atomic layer deposition (ALD) and molecular beam epitaxy (MBE), and explore the formation of ALD-La_2O_3 films on GaN(0001). An island growth mode (Volmer-Weber growth) was observed when La_2O_3 films were deposited directly on GaN(0001) at 250 °C by ALD using tris(N,N'-diisopropylformamidinato)-lanthanum as the precursor and H_2O as the co-reactant. Only with use of a thin template layer, 2 nm-thick hexagonal La_2O_3 grown by MBE or 3 nm-thick cubic Er_2O_3 grown by ALD, can a 2-dimensional ALD-La_2O_3 thin film be formed. The 2-dimensional ALD-La_2O_3 growth on templated-GaN(0001) was confirmed by RHEED and AFM. The macrostructure and microstructure of ALD-La_2O_3 films were verified with XRD, STEM, and atomic structure modeling. The ALD-La_2O_3 film retains a cubic structure on ALD-Er_2O_3 templated-GaN(0001) while it transforms from the cubic phase to mixture of cubic and hexagonal phases on MBE-La_2O_3 templated-GaN(0001) when the film is thicker than 15 nm. Hexagonal La_2O_3 is more thermodynamically stable than cubic bixbyite La_2O_3; the stabilization of cubic ALD-La_2O_3 on ALD-Er_2O_3 templated-GaN(0001) can be attributed to the use of the cubic ALD-Er_2O_3 template and relatively low growth temperature. Analogies are presented for the In_2O_3 system, which has similar cubic bixbyite and hexagonal structures as La_2O_3, except the phases are reversed in In_2O_3. We calculate the surface energy of hexagonal In_2O_3 and compare the result with reported cubic In_2O_3 values to explore the relative contribution of bulk and surface energies in stabilizing the structure of thin crystalline films. Stabilization of thin cubic ALD-La_2O_3 on hexagonal MBE-La_2O_3 templated-GaN(0001) is attributed to likely surface energy differences between cubic and hexagonal La_2O_3.

Plasma Science and Technology Division
Room Union Station B - Session PS-TuP

Plasma Science and Technology Poster Session

PS-TuP2 Low-temperature Atmospheric Plasma Deposition of Photocatalytic Doped Anatase TiO_2 Coatings on Polymer Substrates, *K. Baba, M. Quesada-Gonzalez, S. Bulou, P. Choquet,* ***Nicolas Boscher,*** Luxembourg Institute of Science and Technology, Luxembourg

Anatase titanium dioxide (TiO_2), one of the most important photocatalytic materials, has met a wide range of applications, including self-cleaning surfaces, environmental purification, water splitting and photovoltaic applications. Many attempts, including doping and noble-metal nanoparticles loading, have been proposed to extend the photocatalytic activity of anatase TiO_2 to the visible range as well as reduce the photo-induced electron-hole pair recombination probability. On the other hand, tremendous efforts have targeted a decrease of the temperature formation and deposition of anatase TiO_2-based thin films.

Due to their undeniable industrial advantages, such as low temperature, low cost, easy implementation and in-line process capabilities, low-temperature atmospheric-pressure plasma processes provide a promising alternative for the low-temperature deposition of functional coatings. In this work, we reported the simultaneous formation and deposition of photocatalytic anatase TiO_2 thin films on polymer substrates using a microwave (MW) plasma source operated at atmospheric-pressure.

We further demonstrate our approach as suitable for the formation of doped anatase TiO_2 thin films. Boron-doped anatase TiO_2 were readily deposited on different substrate such as glass, silicon and polymeric optical fibers in a one-step process. The careful selection of the titanium and boron precursors allows the deposition of well adherent, dense and crystalline B-TiO_2 with a visible light activity. The photocatalytic activity of the deposited films was demonstrated by monitoring de degradation of stearic acid or methylene blue under UV and visible light by FTIR and related to the narrowing of the band gap observed by UV-Vis spectrophotometry. Finally, light-diffusing polymer optical fibers were coated using the developed method for the elaboration of a water decontamination reactor for the removal of organics and antibiotics.

PS-TuP3 Radical Nitriding of Silicon Surface Promoted by Surface Plasmon Resonance of Gold Nanoparticle Catalyst, ***Machiko Miyake****, T. Kitajima, T. Nakano,* National Defense Academy, Japan

In recent years, the catalytic effect of gold nanoparticles has attracted attention[1, 2]. We have applied the catalytic property of gold nanoparticles to plasma surface reaction, and aim at the formation of a high-quality ultra-thin film by low damage nitriding by radical (R). This time, we compare the degree of nitridation by the presence or absence of ion irradiation (I), light irradiation (L), and the gold nanoparticle catalyst (C), respectively, and discovered the radical nitriding phenomenon by surface plasmon resonance of gold nanoparticles.

Gold is deposited for two minutes by electron beam evaporation on a SiO_2/Si(100) substrate in an ultra-high vacuum chamber.

Next, 30 mTorr of nitrogen plasma was generated in the attached chamber, and radicals (R) that had passed through a 30 line/inch SUS304 single mesh were irradiated to the sample for 5 minutes. When no light was applied, the sample surface was rotated 90 °.

The AFM images of gold nanoparticles produced by evaporation were compared under irradiation conditions of radicals, light, and ions.

The effect on the shape of gold nanoparticles increased in the order of RILC> RLC> RC.

It is clear that it is necessary to remove the ion irradiation in order to make the effect of the gold nanoparticles.

Next, surface atomic compositions by XPS were compared. The nitrogen ratio was not largely dependent on the irradiation conditions, but was relatively high in RI and RILC conditions where radical and ion irradiation occur simultaneously.

Comparing the XPS N1s spectrum, a peak near 398 eV of SiN is obtained strongly under the RLC condition where surface plasmon resonance can occur, and it can be imagined that a Si-N bond could be formed with the aid of the catalytic activity of Au nanoparticles.

When there is no light irradiation, the signal intensity of the Si-N bond is weak.

Also in the Si2p spectrum of XPS, the chemical shift between SiON and Si is small (3.6 eV) under the RLC conditions, which reflects the formation of the Si-N bond.

From the above, in the presence of light irradiation, it is considered that the catalytic activity of the Au nanoparticles is expressed by the effect of surface plasmon excitation, and the formation of the Si-N bond is promoted.

1. X. Chen, H.-Y. Zhu, J.-C. Zhao, Z.-F. Zheng, and X.-P. Gao, Angew. Chem. 120, 5433 (2008).

2. S. Bhaviripudi, E. Mile, S.A. Steiner, A.T. Zare, M.S. Dresselhaus, A.M. Belcher, and J. Kong, J. Am. Chem. Soc. 129, 1516 (2007).

PS-TuP4 Development and Characterization of a Small-Scale Helical Dielectric Barrier Discharge for Studying Plasma-Surface Interactions, ***Nazli Turan****, P.M. Barboun, W.F. Schneider, J.C. Hicks, D.B. Go,* University of Notre Dame

The study of plasma-surface interactions is an emerging field for a wide variety applications, including sustainable energy (catalytic H2 production), environmental remediation (water purification), medicine (sterilization), and high-value manufacturing (nanomaterial synthesis). These applications are driven by species created in the plasma or at a plasma-surface interface, such as free electrons, gaseous ions, excited molecules and radicals, driving chemistry at a surface. Here, we develop a new dielectric barrier discharge (DBD) configuration to produce surface DBDs over a three-dimensional geometry. The motivation for this geometry was to embed the plasma source inside a packed bed (e.g., catalyst) reactor that had tight spatial restrictions so that it could be implemented in a commercial Fourier transform infrared (FTIR) spectrometer instrument.

The design, which we term a helical DBD, was inspired by surface DBD configurations often employed in plasma actuators for fluid dynamics applications. However, rather than using a 2D surface common in plasma actuators, the helical DBD uses the 3D surface of a cylinder as its dielectric, allowing for greater plasma coverage and in this case, greater interaction with a packed bed. This study characterizes the electrical properties of the helical DBD in both free space and within a packed bed reactor. Various electrical parameters, including energy, deposited power, and plasma current are measured as a function of frequency and voltage. Visual properties are presented to show how the DBD spreads along the dielectric surface or into the packed bed. The effect of being immerged in a packed bed is quantified and the potential future prospects of this type of DBD geometry are discussed.

PS-TuP5 Characteristics of Magnetized High Density Plasma and its Applications, ***Jung-Hyung Kim****, H.C. Lee, D.J. Seong,* Korea Research Institute of Standards and Science, Republic of Korea

We developed high density plasmas in a very uniform magnetic field. To maximize the electron density and efficiency, aspect ratio of discharge cylinder is varied. The discharge pressure is about mTorr or sub-mTorr. Characterization of fully ionized high density helicon plasma is made with probes and optical emission spectra. A helicon plasma with 10^{13} cm^{-3} density is produced in a diameter of 10 cm and length of 70 cm, and the preliminary results of plasma properties are briefly described. The electron temperature is relatively high and the ions are highly ionized. These low pressure plasmas emit short wavelength lights. We inject Xe gas and/or Sn in this system to see the possibility for EUV light sources as one of applications. Weak EUV emission can be detected in low pressure high density magnetized plasma with Sn injection. We could see the possibility for EUV source with this magnetized plasma system. Hereafter, we need more RF power and higher magnetic field to more confine the high density plasma column. We need also to stabilize the plasma for stable strong EUV source at low pressure and high magnetic field.

PS-TuP6 The Effect of Ionic Strength on the Absorption Spectrum of Plasma-Injected Solvated Electrons, ***Daniel Martin****, H.E. Delgado, D.M. Bartels, P. Rumbach, D.B. Go,* University of Notre Dame

The study of plasma-liquid interactions is an emerging field with multifarious applications that are driven by chemical species created in the plasma or at the plasma-liquid interface, such as the hydroxyl radical (OH), hydrogen peroxide (H_2O_2), and, in particular, solvated electrons (e_{aq}^-). The solvated electron is an electron in a polar solution, loosely confined in a potential well formed by the solvent molecules, and notable for being a powerful reductant. Historically, solvated electrons have been studied by using pulse radiolysis and laser photolysis. However, recently we confirmed their presence in a direct current (DC), atmospheric pressure, liquid anode discharge using phase-locked, total internal reflection absorption

spectroscopy (TIRAS). The measured absorption spectrum appeared to be blue shifted from the well-established dilute solution spectrum, and one possible explanation is that the local ionic strength in the double layer at the plasma-liquid interface alters the solvation potential well via increased Coulombic interactions. In this work, we use TIRAS to measure the absorption spectrum as a function of the solution ionic strength and compare the results to measurements produced using pulse radiolysis in order to resolve any differences in the spectra of plasma-injected and bulk-produced solvated electrons.

PS-TuP7 Inductively Coupled Plasma Reactive Ion Etching of Copper Thin Film using Organic Chemicals and Alcohols, ***Moon Hwan Cha**, E.T. Lim, J.S. Ryu, C.W. Chung,* Inha University, Republic of Korea

To improve the performance of Semiconductor memory device, it is important to reduce RC delay. Copper is widely used as interconnect material because it has lower resistivity and higher electromigration resistance than aluminum. However, the conventional dry etching of copper is very difficult due to low vapor pressures of copper compounds and/or low reactivity of copper . As an alternative to dry etching for copper interconnect, a damascene process has been developed in the early 1990s and has been used until now. However, as the device critical dimension continues to shrink, especially below about tens of nanometers, the resistance of the device increases and the performance of the device is deteriorated. As a result, the development of a conventional dry etch process is inevitable.

In this study, new copper etching process which utilizes organic chemicals and alcohols are studied. The etch characteristics of copper under these gases are investigated using inductively coupled plasma reactive ion etching (ICPRIE) as a function of gas concentration and the effects of main etch parameters such as ICP power, dc-bias voltage to substrate, and process pressure are also examined. The etch profiles are observed using FESEM and the etch products formed during etching are analyzed using X-ray photoelectron spectroscopy (XPS), Energy dispersive X-ray spectroscopy (EDS) is also carried out to indentify the etch residues. Plasma characteristics are analyzed using optical emission spectroscopy (OES) and Langmuir probes.

PS-TuP8 High Resolution Quadrupole Mass Spectrometry Analysis for Fusion Reactor and Plasma Facing Materials, *G. Thier, **Brian Regel**, L. Kephart,* Extrel CMS

Fusion reactions break down gaseous hydrogen electrically, forming a plasma. Plasma particles heat up to fusion temperatures and create fusion reactions, releasing huge amounts of energy. Fusion reactors such as tokamaks use tiles made of Tungsten for the interior section exposed to the highest heat and particle fluxes. A major goal of research into fusion materials testing involves exploring material performance in deuterium, helium, or mixed plasmas. The ability to effectively measure helium and deuterium in plasmas simulating fusion plasmas or the effect on plasma facing materials after exposure to such plasmas through techniques such as TDS and TPD is critical to developing our understanding proposed materials' suitability for long-term use in fusion and other plasma facing applications. An Extrel VeraSpec HRQ (High Resolution Quadrupole) Mass Spectrometer was used for the analysis of gas phase components expected in fusion reactions. A certified cylinder containing helium and deuterium was leaked into the vacuum chamber to characterize the long term mass stability of the system under high resolution conditions. This gas was then diluted to determine the low detection limits of these species under the same conditions. A certified cylinder containing carbon monoxide and nitrogen was also leaked into the vacuum chamber to assess the system's ability to resolve the spectrum of this mixture. Spectra at six hour time intervals were taken of the helium and deuterium mixture over 24 hours. The experiment demonstrated that, under high resolution conditions, no detectable mass spectral changes were observed. Diluting the mixture, detection limits of approximately 10ppm (parts per million) were calculated for helium and deuterium. Quadrupole mass spectrometry provides a low cost, simple experimental setup to monitor the effects of fusion reactions on reactor materials.

PS-TuP9 Controlled Layer-by-Layer Etching of Copper Thin Films, ***Eun Taek Lim**, J.S. Ryu, M.H. Cha, C.W. Chung,* Inha University, Republic of Korea

As the critical dimensions of semiconductor devices are reduced for their high performance, fast operating speeds and low operating power, aluminum interconnects are no longer used as a suitable electrode material, but instead of aluminum, the use of copper is increasing. Copper is known as an excellent interconnect material compared to aluminum due to its very low resistance and less electromigration phenomena that cause wire deformation and breakage. However, the damascene process presents some limitations in delineating fine patterns below tens of nanometers. To solve these fatal issues related with the damascene process, intensive researches about copper patterning has been performed using conventional dry etching. Currently, one promising way to etch copper films is cyclic etching. Cyclic etching, including surface modification and its removal, can effectively provide a good etch performance of silicon material. This etching technique is proceeded by inducing surface reactions and precise removal of the modified surfaces, resulting in the accurate control of the etch depth. These results are due to the nature of the self-limiting process and the removal of layers by layer. Various combinations of gases are possible for cyclic etching of the films

In this study, a two-step sequential cyclic etching of surface modification and ion bombardment are investigated. Surface modification and etch depth of the copper film are confirmed using a surface profilometer, a scanning probe microscope and a field emission scanning electron microscope (FESEM) as a function of various parameters such as the conditions of surface modification and bombardment energy of ions. In addition, etch profiles and etch mechanism of copper films in cyclic etching have been studied by FESEM, FETEM and X-ray photoelectron spectroscopy.

PS-TuP10 Effects of Bias on Quasi-Atomic Layer Etching of Silicon Dioxide by Cyclic Ar/C_4F_8/O_2 and Ar Plasmas, ***Xifeng Wang**,* University of Michigan; *M. Wang, A. Mosden, P.E. Biolsi,* TEL Technology Center, America, LLC; *M.J. Kushner,* University of Michigan

With the reduction in feature size in microelectronics fabrication, the process flow in plasma etching includes several steps that are devoted to producing the mask that is ultimately used to define the semiconductor (or dielectric) critical dimension (CD). These processes include tight pitch/space and multi-layer structures composed of several materials which, in turn, require a sequence of recipes steps to etch. In this regard, atomic layer etching (ALE) is being employed in several steps of the process flow to improve CD tunability and resist selectivity.

In this work, we report on a computational investigation of the ALE plasma etching of dielectric (silicon dioxide) layers in multi-layer structures using a cyclic fluorocarbon mixture deposition and Ar etching process. Reactor scale modeling was performed using the Hybrid Plasma Equipment Model (HPEM) and feature scale modeling was performed by Monte Carlo Feature Profile Model (MCFPM). The first step in the process largely deposits fluorocarbon polymer. The second step activates the etch. The reactor is a multi-frequency capacitively coupled plasma (CCP) augmented by a DC bias to the top electrode. During the deposition step where ion energies should be low, 40 MHz source power is applied to the bottom electrode and a 900 V negative DC bias is applied to the top electrode. For the etch step where moderately energetic ions are desired, only a 10 MHz bias is applied to the bottom electrode.

During the deposition step, ion energies to the wafer are typically lower than 40 eV. These low energy ions activate surface sites (but typically do not sputter), which then enables deposition of a controllable thickness of polymer. During the etch step, the flux of Ar^+ at the surface is at about 1.4 10^{15} $cm^{-2}s^{-1}$, when then requires several to ten of seconds to remove a monolayer or several monolayers of dielectric. Since the layers being removed are at the bottom of a high-aspect-ratio feature, it is desirable to narrow the angular distribution of the ions by increasing bias power which then also increases ion energy. The narrower distribution works towards maintaining the CD, however the higher ion energy works against maintaining the quasi-ALE character of the etch. Tradeoffs between simultaneously maintaining CD and quasi-ALE performance will be discussed .

* Work supported by Tokyo Electron Ltd. and the US Department of Energy Office of Fusion Energy Science.

PS-TuP11 Electron Beam Generated Produced Plasmas Produced in Oxygen: Measurements and Simulations, ***Scott Walton**, D.R. Boris,* U.S. Naval Research Laboratory; *S. Rauf,* Applied Materials, Inc.

The U.S. Naval Research Laboratory (NRL) has developed a processing system based on an electron beam-generated plasma. Unlike conventional discharges produced by electric fields (DC, RF, microwave, etc.), ionization is driven by a high-energy (1-3 keV) electron beam, an approach that can yield very different plasma properties than conventional plasma processing systems. Electron beam-generated plasmas are broadly 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. When produced in oxygen

backgrounds, this combination of features leads to a surprisingly large density of O^+ ions. In this work, we combine plasma diagnostics and modeling to characterize the spatial evolution of electron beam generated plasmas produced in oxygen as a function of operating parameters such as beam energy, beam current and pressure. Measurements of ion fluxes at adjacent surfaces indicate the large O^+ ion densities can lead to O^+/O_2^+ flux ratios that far exceed one. The modeling results capture salient features of the plasma and provide a better understanding of plasma kinetics that lead to the measured ion flux ratios. This work is partially supported by the Naval Research Laboratory base program.

PS-TuP12 Silicon Micro-Channel Definition Via ICP Plasma Etching Process Using Different Hard Masks*, H.S. Alvarez, J.A. Diniz, C.S. Ruiz, A.R. Silva, F.H. Cioldin,* UNICAMP, Brazil*; **Valter S.N. Junior**,* USP - EESC, Brazil

Alumina, pieces of silicon wafers, lithographed aluminum (Al) and aluminum nitride (AlN) were used as mechanical hard masks materials for micro-channel etching in silicon (Si) using a high-density inductively coupled plasma - Reactive Ion Etching (ICP-RIE) reactor. The mechanical masks of alumina and silicon, with thickness of 1 mm and 0.35 mm, respectively, were positioned manually on the Si substrates, where the silicon micro-channels (SiMCs) were etched. In the case of Alumina, two rectangular masks were spaced 0.7 mm between them in the Si substrate, resulting in only one micro-channel. For Si mask, six Si pieces with rectangular shapes were positioned in the Si substrate with different spacing between them. The Al films with thickness of 500 nm were evaporated and wet etched using a two lithographed masks patterns: i) parallel lines with width of 0.8 mm and 0.2 mm spaced ; ii) parallel lines with width of 0.2 mm and 0.8 mm spaced. This second sample was carried out to an ICP plasma nitridation (for 30 minutes) to result an AlN/Al structure. AlN material is considered a hard mask especially for the RIE plasma etching based on SF6 gas. The ICP-RIE processes to fabricate the SiMC and to characterize the mask resistance under the plasma etching were carried out using these fixed parameters: 10 sccm of SF_6 + 15sccm of Ar, 15 mTorr of process pressure, 1200W of ICP and 40W of RIE powers. The SiMC profiles, obtained by scan profiler system. indicate that: (i) with alumina mechanical masks, SiMC was obtained the maximum depth value of 108 µm, for the width of 0.7 mm. As in this case, it has only one channel, the unprotected silicon region was small when this sample is compared with others. Small silicon region to etch, highest etch rate can be obtained; (ii) with silicon mechanical masks, it was obtained the depth values between 53 and 87 µm. Furthermore, it can be observed that there is a dependence between the width and the depth of channel. (iii) with Al mask defined by lithography and etching, the SiMC profiles are uniform, with the same width and depth of about 0.24 mm and 80 µm, respectively. The spacing regions with width of 0.76 mm are with surface roughness (up to 5 µm), indicating that the Al mask has not supported the plasma etching for 2 hours; (v) with AlN/Al mask defined by lithography, etching and plasma nitridation, the SiMC profiles are uniform, with the same width and depth of about 0.33 mm and 90 µm, respectively. The spacing regions with width of 0.66 mm have not presented the surface roughness, indicating that the Al mask has supported the plasma etching for 2 hours. However, at the end of plasma etching, this mask was very thinner.

PS-TuP13 Corrosion Barrier Coatings for Aerospace Materials Deposited by Atmospheric Pressure CVD*, **Dhruval Patel**, Z. Jeckell, T. Choi, D.E. Barlaz, L. Bonova, D.V. Krogstad, D.N. Ruzic,* University of Illinois at Urbana-Champaign*; S. Chaudhuri,* University of Illinois at Chicago

Rigorous performance standards for tactical vehicles and aircrafts demand the use of chemical

processes to apply a galvanic corrosion barrier coating. Current processes are often hazardous and

environmentally unsafe as they involve chemicals such as hexavalent chromium. The handling and

disposal of the waste products of these wet chemical processes puts a significant financial burden on the

Department of Defense. This work aims to design and develop a process which employs an atmospheric

pressure plasma jet to substitute the wet chemical processes. The proposed project focuses on

depositing zirconia-silica conversion coatings on aluminum surfaces as a corrosion barrier. The process

utilizes existing chemical vapor deposition precursors with a much smaller chemical foot print. The

process is capable of depositing 100 – 300 nm zirconia-silica layers with relatively low carbon content

as observed under XPS. Initial tactical testing showed reduced water intrusion for painted silica coated

substrates.

PS-TuP14 Atmospheric Pressure Plasma: An Alternative Tool for the Synthesis of Efficient Photocatalytic Materials*, **Amal Sebastian**,* University of Notre Dame

Photocatalytic splitting of water into hydrogen and oxygen is a method to convert solar energy into storable chemical energy directly, and it has received significant attention for its high potential for low cost and clean energy production. Developing efficient and cost-effective photocatalysts for water splitting is a growing need for solar energy research. In this work, we propose an alternative method to deposit photocatalytic materials with atmospheric pressure plasma (APP). The design and experimental approach for depositing the visible light photoelectrode TaOxNy using APP with a suitable solution precursor are explained in detail. The effect of plasma parameters on the composition of films is investigated by monitoring the surface chemistry changes with X-ray photoelectron spectroscopy. The observed changes in the composition of films with modulation of plasma parameters hint towards alternative processing routes to deposit photocatalytic materials efficiently

PS-TuP15 Synthesis of Functional Polydopamine using Atmospheric Pressure Plasmas*, **Yun Jong Jang**, M.K. Mun, J.E. Kim, D.W. Kim, G.Y. Yeom,* Sungkyunkwan University, Republic of Korea

Dopamine, known as a monoamine neurotransmitter, has functional groups such as catechol and amine. Under the state of oxidant and alkaline, the dopamine go through self-polymerization and creates polydopamine. This polymer is known to exhibit excellent adhesion (known as a mussel-inspired adhesive) to most of all organic and inorganic material surfaces. In this study, by using atmospheric pressure plasmas (dielectric barrier discharges; DBDs) with a low electron energy and a dopamine solution mist formed by piezoelectric module, a possibility of depositing functional polymer films showing the physical and chemical characteristics of polydopamine without breaking the functional group of the dopamine has been investigated for different plasma voltages. By using the lower DBD voltage of 1.5 kV, the partial dissociation of dopamine molecule for polymerization without breaking the catechol/amine functional groups of dopamine could be achieved while the use of the higher DBD voltage to 3.0 kV tends to break more functional groups of dopamine into atoms which leads to the decreased physical and chemical characteristics of polydopamine. It is believed that this atmospheric pressure plasma polymerization method of dopamine can be applied to various areas which require surface modifications instantly by forming a polydopamine film similar to the wet methods.

PS-TuP16 Effect of $C_x(x=4\sim7)F_8$ on the Etch Properties in Inductively Coupled Plasmas*, **Hyun Woo Tak**, D.I. Sung, Y.J. Shin, D.W. Kim, G.Y. Yeom,* Sungkyunkwan University, Republic of Korea

In semiconductor industries, the trend of scaling down is ongoing in ultra large scale integrated (ULSI) devices such as logic devices or 3D NAND devices. To achieve the scaling down of the devices, multiple patterning technologies such as double patterning technology (DPT) and quadruple patterning technology(QPT) have become essential technologies and require a high selective SiO_2 etch process. In this study, three types of perfluorocarbon (PFC) precursors(C_4F_8, C_5F_8 and C_7F_8)were used and the effects of these PFCs on the etch characteristics of SiO_2, Si_3N_4, and ACL and their etch selectivities were investigated by using $C_x(x=4\sim7)F_8/Ar/O_2$ plasmas. Among these, C_5F_8 and C_7F_8 are liquid phase at room temperature and, to deliver these liquid precursors to the process chamber,the inductively coupled plasma (ICP) system was equipped with a constant temperature heated canister and heated gas lines. The etch results showed that the selectivities of SiO_2/Si_3N_4 and SiO_2/ACL with $C_7F_8/Ar/O_2$ plasmas were much higher than those with $C_4F_8/Ar/O_2$ and $C_5F_8/Ar/O_2$ at the optimized etch conditions. It is found that, with $C_7F_8/Ar/O_2$ plasmas, lower F radicals in plasmas and thicker fluorocarbon polymers on material surfaces were formed. Furthermore, $C_7F_8/Ar/O_2$ plasmas exhibited more anisotropic SiO_2 etch profiles than the plasmas generated with $C_4F_8/Ar/O_2$ and $C_5F_8/Ar/O_2$.

PS-TuP19 Plasma Etching High Aspect Ratio Carbon Nanotube Structures for a Neural Probe*, **Spencer Roberts**, G. Chen,* Brigham Young University

A new approach to neural probe arrays using Carbon Nanotube Templated Microfabrication produces probes that would be smaller and more

compliant than existing technologies. To achieve tall, straight probes, a sacrificial hedge is grown connecting adjacent probes and then is removed with a series of plasma etching conditions. These etches are challenging due a number a factors, including the variability in samples, the density function of the probes, and high aspect characteristics of the structure. Previously we developed a process that allowed us to selectively remove the hedges and leave the probes intact. We have now quantified and refined that process.

PS-TuP20 NO_x Fixation by Atmospheric Pressure N_2/O_2 Filamentary DBD Plasma over Water: Physicochemical Mechanisms of Plasma-Liquid interactions*, **Nepal Roy**, C. Pattyn,* Université libre de Bruxelles, Belgium*; A. Remy, N. Maira, F. Reniers,* Université Libre de Bruxelles, Belgium

NO_x formation from N_2/O_2 gas or air through nonthermal plasmas has become an important research topic for researchers in the last decades, considering both environmental and industrial importance. In this study, an atmospheric pressure filamentary dielectric barrier discharge (DBD) plasma has been produced over the water surface by a sinusoidal20-30 kV, 24.5 kHz power supply. In order to study the physicochemical mechanism of plasma-liquid surface interaction for NO_x production, the characterization of the plasma has been performed using optical emission spectroscopy (OES) and by recording voltage-current curves (with a high voltage probe, a Rogowski coil and a digital oscilloscope). The concentration of nitrates and nitrites ions in water was determined by ion chromatography. The power absorbed by the plasma discharge has been determined by Volt-Charge (V-Q) Lissajous curves in different experimental conditions. It is shown that the absorbed power increases sharply with increasing applied voltage and with the content of N_2 in the gas mixture. OES diagnostics allows identifying the exited species, to study the relative emission intensity of NO (A-X) while varying the plasma gas composition, and to determine the rotational (T_{rot}≈320-380 K) and vibrational (T_{vib}≈2600-3800 K) temperatures under different experimental conditions. The Boltzmann plot method has been employed for the estimation of T_{rot} and T_{vib} by using the OH (A-X) and the N_2 (C-B) bands respectively. Both Trot and T_{vib} increase with increasing applied voltage and with increasing the O_2 content in the gas mixture. In the liquid phase, the concentration of NO_2^- is maximum at low applied voltages, treatment times and with pure N_2 discharges, whereas in these conditions the concentration of NO_3^- is minimum. The concentration of NO_3^- increases with increasing treatment times, applied voltages and O_2 content in the gas mixture. It is shown that the nitrites formed during the plasma treatment transform rapidly, and completely into nitrates. From the total amount of nitrites and nitrates synthesized in solution (named NO_x below), the energy yield for the conversion was estimated. Depending on the starting gas composition and applied powers, yields of ~180 W/mg NO_x to ~ 9.5 W/mg NO_x were obtained.

PS-TuP21 Simulation Study of Capacitively Coupled Radio Frequency Silane/Hydrogen Plasma Discharges - Effect of Tailored Voltage Waveforms*, S.W. Huang, **Keh-Chyang Leou**,* National Tsing Hua University, Taiwan, Republic of China

Capacitively coupled plasma discharges (CCP) have been widely employed for material processing, such as etching and deposition. The purpose of this study is to investigate the effect of tailored voltage waveforms (TVWs) on the plasma characteristics of SiH_4/H_2 plasmas, typically, for Si film deposition. A fluid model based numerical simulation analysis (CFD-ACE+) is employed to investigate the basic discharge characteristics and corresponding basic physical and chemical mechanisms occurring in the plasma reactor. The TVWs adopted in this study are formed by four harmonics of 13.56 MHz sinusoidal voltages. Different voltage waveforms can be generated by tuning the relative phase between the four frequencies. A peak or valley voltage waveform is obtained when the "phase" is 0 or π, respectively. Simulation results show that the “peak” waveform results in a lower sheath voltage, and the SiH_2/SiH_3 flux ratio reaching the substrate is 40% lower than that for CCP with single frequency of 13.56 MHz. Thus, by using TVWs, it is possible to fine tune the structure and/or property of the deposited Si film. The detailed results of the simulation analysis of CCPs with TVWs will be presented.

*Acknowledgement : Work supported by the MOST, Taiwan/ROC.

Atomic Scale Processing Focus Topic
Room B130 - Session AP+BI+PS+TF-WeM

Surface Reaction Analysis and Emerging Applications of Atomic Scale Processing

Moderator: Eric A. Joseph, IBM T.J. Watson Research Center

8:00am **AP+BI+PS+TF-WeM1 Open Spaces in Al_2O_3 Film Deposited on Widegap Semiconductors Probed by Monoenergetic Positron Beams***, **Akira Uedono**,* University of Tsukuba, Japan*; T. Nabatame,* NIMS, Japan*; W. Egger, T. Koschine,* Universität der Bundeswehr München, Germany*; C. Hugenschmidt, M. Dickmann,* Technische Universität München, Germany*; M. Sumiya,* NIMS, Japan*; S. Ishibashi,* AIST, Japan **INVITED**

Positron annihilation is a useful technique for characterizing vacancy-type defects in semiconductors, and it has been successfully used to detect defects in GaN. This technique is also useful for detecting open spaces in thin amorphous films deposited on semiconductor substrates. When a positron is implanted into condensed matter, it annihilates with an electron and emits two 511-keV gamma quanta. The energy distribution of the annihilation gamma rays is broadened by the momentum component of the annihilating electron-positron pair. A freely diffusing positron may be localized in a vacancy-type defect because of Coulomb repulsion from positively charged ion cores. Because the momentum distribution of the electrons in such defects differs from that of electrons in the bulk material, these defects can be detected by measuring the Doppler broadening spectra of the annihilation radiation. Because the electron density in open spaces or vacancy-type defects is lower than that in the bulk, the lifetime of positrons trapped by such regions is longer than that of positrons in the delocalized state. Thus, the measurement of the positron lifetime also provides information of open spaces and vacancies in solid. In the present work, open spaces and defects in the Al_2O_3(25 nm)/GaN structure were probed by using monoenergetic positron beams.

Al_2O_3 films were deposited on GaN by atomic layer deposition at 300ºC. Temperature treatment above 800°C leads to the introduction of vacancy-type defects in GaN due to outdiffusion of atoms from GaN into Al_2O_3. The width of the damaged region was determined to be 40-50 nm from the Al_2O_3/GaN interface, and some of the vacancies were identified to act as electron trapping centers. In the Al_2O_3 film before and after annealing treatment at 300-900ºC, open spaces with three different sizes were found to coexist. The density of medium-sized open spaces started to decrease above 800°C, which was associated with the interaction between GaN and Al_2O_3. Effects of the electron trapping/detrapping processes of interface states on the flat band voltage and the defects in GaN were also discussed.

The present research suggests that the interaction between amorphous Al_2O_3 and GaN introduces not only vacancy-type defects in GaN but also changes the matrix structure of Al_2O_3 film. We also revealed that the electron trapping/detrapping processes of interface charge states are influenced by the defects introduced in GaN.

8:40am **AP+BI+PS+TF-WeM3 Surface Reaction Analyses of Atomic-layer Etching by Controlled Beam Experiments***, **Kazuhiro Karahashi**, T. Ito, S. Hamaguchi,* Osaka University, Japan

In manufacturing of modern advanced semiconductor devices such magnetoresistive random-access memories (MRAMs), phase-change random-access memories (PRAMs), and three-dimensional integrated circuit (3D IC) devices, damage-free high-precision etching for various materials is an indispensable process technology. Halogenation of a surface layer combined with low-energy ion bombardment or ligand-exchange of organic molecules for the formation of metal complexes is a surface reaction that may be used for such highly selective etching processes with atomic-scale precision. A better understanding of surface reactions taking place during the etching process often allows one to control and optimize the process more effectively. In this study, we have developed a new surface-reaction analysis system with highly controlled beams of various species and examined surface reaction mechanisms of plasma-assisted or thermal atomic-layer etching (ALE) processes for silicon (Si), copper (Cu), and nickel (Ni) films. The beam experiment of this system offers an experimental "simulation" of actual ALE surface reactions. The system is equipped with differentially-pumped multiple beam sources that can irradiate the sample set in an ultra-high-vacuum (UHV) chamber with different types of beams, i.e., low-energy ions, thermal molecules, metastable radicals, and atomic/molecular clusters, independently. During the beam irradiation, scattered and desorbed species may be measured by a differentially pumped quadrupole mass spectrometer (QMS). Time-resolved measurements of QMS synchronized with pulsed beam irradiation facilitate detailed analysis of the beam-surface interactions. Chemical states of adsorbed species on the sample surface may be measured by X-ray photoelectron spectroscopy (XPS). In this presentation, we discuss the mechanisms of halogenated-layer formation on the Si, Cu, or Ni surfaces by their exposure to XeF2 or Cl2 gases and the removal mechanisms of halogenated species from the surface by low-energy ion irradiation or surface heating. Thermal desorption mechanisms of Cu or Ni by the metal-complex formation with organic molecules (such as diketones) from its oxidized surface are also discussed

9:00am **AP+BI+PS+TF-WeM4 Surface Reaction Analysis of Fluorine-based Reactive Ion Etching (RIE) and Atomic Layer Etching (ALE) by Molecular Dynamics (MD) Simulation***, **Erin Joy Tinacba**, M. Isobe, K. Karahashi, S. Hamaguchi,* Osaka University, Japan

Plasma etching has always been a useful process in semiconductor device fabrication. There are several ways of using plasma etching such as reactive ion etching (RIE), wherein the material surface is bombarded with energetic ions while it also exposed to chemically reactive radicals from the plasma. Because of the energy provided by bombarding ions and high chemical reactivity on the surface, the surface is etched even at a relatively low temperature due to the combination of physical and chemical sputtering effects. RIE is often suited to fast etching processes of high aspect ratio structures since it can provide high etching yields. Another application of plasma etching is plasma-assisted atomic layer etching (ALE), wherein chemical and sputtering effects of typical plasma etching are separated into two steps. In a typical ALE process, the first step is an adsorption step wherein chemically reactive molecules or radicals from a plasma are used to modify the material surface. The modified monolayer or a thin layer on the material surface is then etched during the subsequent desorption step (second step) where low-energy ions bombard the surface. The etching reaction stops when the modified layer is depleted. This cycle is repeated many times until the desired etched depth is reached. The ALE process might be slow but it can provide tight control in the etch variability for sub-10 nm technology applications.

In this paper, molecular dynamic (MD) simulation is used to understand the effects of ions and radicals of high fluorine (F) content on etching reactions of silicon (Si), silicon dioxide (SiO_2), and silicon nitride (Si_3N_4), which may be observed in RIE processes based on, e.g., SF_6, C_2F_6, or NF_3 plasmas. If such a plasma is used as a radical source and ion bombardment steps by inert gas ions are separated from the radical exposure steps, an ALE process may be performed with similar surface reactions. In typical RIE, a supply of a large amount of fluorine to the surface by increasing the flux of energetic ions containing multiple F atoms (such as SF_5^+, $C_2F_5^+$ and NF_2^+ ions) and/or by increasing a F radical flux to the surface results in high etch rates. It has been found that the etching rates by such highly fluorinated ions obtained from MD simulations are in good agreement with experimental observations and the deep fluorination of the surface accounts for their high etch rates. Although fluorine may be considered too corrosive to be used for ALE, we also analyzed by MD simulation an ALE process by fluorine-containing radicals such as NF2 and compared the results with experimental observations.

9:20am **AP+BI+PS+TF-WeM5 Analysis of Metal Surface during Atomic Layer Etching with Gas Cluster Ion Beam and Organic Acid***, **Noriaki Toyoda**, K. Uematsu,* University of Hyogo, Japan

Surface states of metal surface after atomic layer etchings (ALE) with gas cluster ion beam (GCIB) and organic acid were investigated using surface analysis tools (mainly X-ray photoelectron microscopy). In recent years, we have reported the usage of GCIB irradiation for the removal steps of ALE. Since GCIBs are aggregates of thousands of gas atoms or molecules, the energy/atoms or energy/molecules can be easily reduced to several eV even though the total energy of GCIB is several keV. This characteristic is beneficial for low-damage irradiation. In additions, since GCIBs induce dense energy deposition, the bombarded area experiences transient high-temperature and high-pressure conditions. As a result, chemical reactions are enhanced at low-temperature. These characteristics are suitable for the removal step in ALE.

In this study, we have investigated the surface state of metal (Ni, Cu) after ALE with GCIB and organic acid using in-situ XPS. Prior to GCIB irradiation, metal surfaces were cleaned by Ar ions. Then Ni or Cu surface were exposed to acetic acids or acetylacetones. The surface layer with adsorbed organic acid on metals were removed by subsequent GCIB irradiation. The difference of the surface states of metal between Ar and O_2-GCIB

irradiation are compared with in-situ XPS results. Etching mechanism by GCIB in the presence of the adsorbed organic acid will be discussed.

9:40am **AP+BI+PS+TF-WeM6 In-situ Characterization of Growth Kinetics of Piezoelectric Films Grown by Atomic Layer Deposition Utilizing an Ultra-high Purity Process Environment**, ***Nicholas Strnad***, General Technical Services, LLC; *D.M. Potrepka,* U.S. Army Research Laboratory; *N. O'Toole, G.B. Rayner,* Kurt J. Lesker Company; *J.S. Pulskamp,* U.S. Army Research Laboratory

Recently, $PbZr_xTi_{1-x}O_3$ (PZT) was grown by atomic layer deposition (ALD) in a piezoelectric film stack that was micro-machined into electrically actuated cantilever beams. [1] ALD PZT is a process technology that may drive 3D PiezoMEMS that utilizes piezoelectric films deposited on micro-machined sidewall structures. AlN is also a desirable piezoelectric for 3D PiezoMEMS but integration has been hampered by its sensitivity to reactive background gases resulting in oxygen contamination of several atomic percent and above. [2] Reactive background gases can also impact oxide films by skewing the non-uniformity and growth-per-cycle (GPC). Thus, individual reactor conditions play a significant role in both the growth kinetics, and resulting quality of thin films grown by ALD. To address both of these issues there exists the need for ultra-high purity (UHP) process capability. Here, we present how the transition from non-UHP to UHP process environment affects ALD AlN and the constituent oxide films in ALD PZT. The UHP process environment also enables the rapid characterization of the reaction kinetics of ALD processes by in-situ ellipsometry. The reaction kinetics of several constituent oxides for ALD PZT are presented based on empirical in-situ observations.

References

[1] Strnad, N.A. (2019) Atomic Layer Deposition of Lead Zirconate-Titanate and Other Lead-Based Perovskites (Doctoral Dissertation) https://doi.org/10.13016/8dqx-7pev

[2] Chen, Z. (2019) Thermal atomic layer deposition of aluminum nitride thin films from AlCl3 (Master's Dissertation)

11:00am **AP+BI+PS+TF-WeM10 Nanoscale Surface Modification of Medical Devices using Accelerated Neutral Atom Beam Technology**, ***Dmitry Shashkov***, *J. Khoury, B. Phok,* Exogenesis Corp. **INVITED**

Controlling surface properties of biomaterials is vital in improving the biocompatibility of devices by enhancing integration and reducing bacterial attachment. We use Accelerated Neutral Atom Beam (ANAB) technology, a low energy accelerated particle beam gaining acceptance as a tool for nanoscale surface modification of implantable medical devices. ANAB is created by acceleration of neutral argon atoms with very low energies under vacuum which bombard a material surface, modifying it to a shallow depth of 2-3 nm. This is a non-additive technology that results in modifications of surface topography, wettability, and chemistry. These modifications are understood to be important in cell-surface interactions on implantable medical devices. Similarly, ANAB could be used to modify surfaces of medical device coatings (small molecules and proteins)., creating a native drug elution barrier. In this study, we characterize the effects of ANAB on several materials including metals (Ti, CoCr) and polymers (PEEK, PP, PVC) and measure the differential ability of eukaryotic versus prokaryotic cell attachment on these modified surfaces. We also study the ability of ANAB to create an elution barrier on a drug coating without the use of binding polymers. We identified that eukaryotic cells including mesenchymal stem cells (MSC) and osteoblasts increase attachment and proliferation on treated surfaces as measured by MTS assay and cell visualization by microscopy. MTS assay shows that by day 14, control PEEK has 9,925±1,994 cells while ANAB-treated PEEK has 88,713±6,118 cells (n=3; $p<0.0014$). At the same time, we find that bacterial cells including *S.aureus* and *P.aeruginosa* have a decreased ability to bind on the ANAB-treated surface. This dichotomy of cellular attachment may be attributed to the nano-scale surface topography, favoring larger eukaryotic cells while inhibiting attachment of smaller bacterial pathogens. In studies focusing on drug elution, rapamycin was spray-coated on the surface of CoCr bare metal stents and either left as control or ANAB-treated the surface of the drug. These stents were then placed in a plasma elution assay for up to 7 days. We found that untreated stents eluted off most of the drug within 24 hours, and 100% of it by 48 hours post-elution. The ANAB-treated stents, however, showed a favorable elution profile slowly releasing the drug over the 7 day period. ANAB, therefore, has many possible uses in medical device technology in increasing integration, decreasing bacterial attachment and potentially biofilm formation, and, if desired, create an elution profile for a combination drug-device without the use of binding polymers.

11:40am **AP+BI+PS+TF-WeM12 Chemically Enhanced Patterning of Nickel for Next Generation EUV Mask**, ***Xia (Gary) Sang***, *E. Chen,* University of California, Los Angeles; *T. Tronic, C. Choi,* Intel Corporation; *J.P. Chang,* University of California, Los Angeles

The ever-increasing demand in high-precision pattern definition and high-fidelity pattern transfer in the IC manufacturing industry calls for continuous advancement in lithography technology. Extreme Ultra-Violet (EUV) lithography is being widely adopted for defining sub-10 nm nodes. Due to its ideal optical properties, Ni is under active research as the future absorbing layer material in EUV masks, the profile of which determines the quality of resulting lithographic patterns. Contemporary techniques for patterning Ni rely on noble ion beam milling, which leaves considerable amounts of re-deposition on feature sidewall. Finding chemically selective patterning technique is thus of critical importance. Due to the etch-resistant nature of Nickel, removal at an atomic level is enabled by chemical modification of the surface through plasma exposure and subsequent introduction of organic ligands. Plausible chemicals are first screened by thermodynamic assessments from available databases, experiments were then conducted to validate the theoretical predictions.

Both blanket and patterned Ni thin films were studied using this reaction scheme. Organic chemistries, such as acetic acid and formic acid were first investigated to determine the feasibility of metal-organic formation through direct exposure. The efficacy of acetic acid and formic acid etching chemistries were confirmed through solution-based studies on Ni, the formation of Ni(CH3COO)2 and Ni(HCOO)2 were confirmed through mass spectrometry. Nickel oxide formation and subsequent removal were confirmed by quantifying the change in the relative intensities of peaks of metallic Ni (852.6 eV) and oxidized Ni (853.7 eV) by X-Ray Photoelectron Spectroscopy (XPS).

The chemical reactivity difference between Ni0 and Ni2+ was quantified in the work to explore the attainable etch selectivity. Due to the decrease in radical concentration and flux, vapor phase etching of metallic Ni resulted in small thickness reduction (~ 0.4 nm/cycle). It is then tested that surface modification, particularly oxidation, is capable of promoting subsequent reactions by lowering reaction energy barrier through metal oxide formation. An oxygen plasma treatment is added prior to acid vapor exposure, and this cyclic approach results in a relatively linear etch rate of ~ 2 nm/cycle, which translates to a 50:1 etching selectivity of NiO over Ni. The same cyclic approach was then applied to patterned samples, post-etch sidewall angle of ~ 85° is measured, which closely conserves the initial feature profile (~ 87°).

12:00pm **AP+BI+PS+TF-WeM13 Surface Reactions of Low Energy Electrons and Ions with Organometallic Precursors and their Relevance to Charged Particle Deposition Processes**, ***Rachel Thorman***, Johns Hopkins University; *E. Bilgilisoy,* FAU Erlangen-Nürnberg, Germany; *S. Matsuda, L. McElwee-White,* University of Florida; *D. Fairbrother,* Johns Hopkins University

Focused electron beam induced deposition (FEBID) and focused ion beam induced deposition (FIBID) are nanofabrication techniques where beams of charged particles (electrons or ions) create metal-containing nanostructures by decomposing organometallic precursors in low pressure environments. Consequently, the interactions of electrons and ions with surface-bound organometallic precursors are fundamental processes in these deposition processes. Previously performed ultra-high vacuum (UHV) studies on low energy (below 100 eV) electron interactions with adsorbed precursors (e.g. $Pt(PF_3)_4$, $MeCpPtMe_3$, and $Co(CO)_3NO$) have revealed that electron-induced reactions of surface bound precursors occurs in two sequential steps: (1) an initial step characterized by precursor decomposition/deposition and partial ligand desorption followed by (2) decomposition of the residual ligands. However, a similar level of understanding does not exist for low energy ion interactions with organometallic precursors. In this presentation, I will show that a low temperature, UHV surface science approach can serve as a platform to study the reactions of both low energy electrons (500 eV) and low energy ions (<1kV Ar^+ ions) with organometallic precursors. Results from *in situ* X-ray photoelectron spectroscopy (XPS) and mass spectroscopy (MS) clearly show that low energy electron and ion-induced reactions of several surface-adsorbed species, including $(\eta^5\text{-}Cp)Fe(CO)_2Re(CO)_5$, $Ru(CO)_4I_2$, $Fe(CO)_5$, and $Co(CO)_3NO$, are markedly different. Similarly to electron-induced reactions, low-energy ion-induced reactions proceed in a two-step process with an initial decomposition step primarily characterized by ligand loss. However, ligand loss is typically must more extensive than is observed for electron-induced reactions; for example, in the case of $(\eta^5\text{-}Cp)Fe(CO)_2Re(CO)_5$ and $Fe(CO)_5$, all CO ligands desorb in this initial step. The second step in the ion induced reactions can be described as a regime

primarily characterized by physical sputtering. These contrasting results are discussed in the context of different deposition mechanisms proposed for FEBID and FIBID.

Plasma Science and Technology Division
Room B131 - Session PS+EM-WeM

Plasma Processing of Materials for Energy

Moderators: Ankur Agarwal, KLA-Tencor, Saravanapriyan Sriraman, LAM Research

8:00am **PS+EM-WeM1 Plasma Processes for High Efficiency Multi-Junction Solar Cells Fabrication***, **Maxime Darnon**, M. Volatier, P. Albert, M. de Lafontaine, P. St-Pierre, G. Hamon,* LN2, CNRS / Université de Sherbrooke, 3IT, Canada*; C. Petit-Etienne, G. Gay, E. Pargon,* LTM, CNRS / Université Grenoble Alpes, France*; V. Aimez, S. Fafard, A. Jaouad,* LN2, CNRS / Université de Sherbrooke, 3IT, Canada **INVITED**

Multijunction solar cells provide the highest efficiency for solar energy conversion into electricity. With record efficiency above 45%, they are used in concentrated photovoltaic systems where their cost is mitigated by the sunlight concentration. Conventional technics for such solar cells' fabrication include III-V materials epitaxy on germanium, electrodes lift off, antireflective coating deposition by physical vapor deposition and isolation by saw dicing. In this presentation, we will show how plasma processes can advantageously be used to replace some of these steps and how it could enable the fabrication of new architectures of solar cells.

A low-damage III-V plasma etching step can isolate the solar cells one to the other before the mechanical saw dicing. This reduces the density of recombination centers at the edge of the solar cells and provides therefore a higher open circuit voltage. Deep germanium plasma etching can also be used for solar cells dicing with trenches as small as 10 µm. As an alternative to physical vapor deposition, plasma enhanced chemical vapor deposition can coat high transparency silicon nitride and silicon oxide that form an excellent anti-reflective coating and passivate surface recombination centers.

In addition to their benefit for conventional solar cells fabrication, these plasma-based processes also provide opportunity for the fabrication of new kinds of multijunction solar cells, such as ultra small solar cells (<0.07 mm^2), front-side contacted solar cells, back-side contacted solar cells, and through cell via contacted solar cells.

8:40am **PS+EM-WeM3 Combinatorial Synthesis of Ternary Oxides by Reactive Sputtering for CdTe Solar Cells***, **Yegor Samoilenko**, G. Yeung, C.A. Wolden,* Colorado School of Mines

Polycrystalline CdTe-based solar cells have reached efficiencies of over 22% in the recent years. The road towards high V_{oc} and 25% devices requires a combination of low interface recombination velocity, higher lifetime, and higher carrier concentration in the CdTe absorber. It was recently demonstrated that the impact of the interface recombination on the performance of the device is more pronounced as carrier concentration and lifetime increase. Magnesium zinc oxide (MZO) has been identified as a transparent emitter that enables high efficiency in CdTe based solar cells. By controlling the alloy composition one may tune the conduction band alignment with CdTe absorber at the front interface to reduce recombination. Most previous work has employed MZO targets sputtered in Ar. However there are open questions as to what the optimal composition, its stability, and sensitivity to subsequent processing.In this work we perform a combinatorial study of MZO buffer layer prepared by co-sputtering of Zn and Mg in oxygen-containing atmosphere. Combinatorial libraries are formed with a band gap variation of more than 0.4 eV across a 2 inch substrate. These are integrated into standard CdTe to determine the optimal composition based on using J-V characteristics. In addition, the stability of these films is assessed by surface spectroscopy, and routes to stabilize performance are introduced.

9:00am **PS+EM-WeM4 Potential Applications of TiN-based Plasmonic Nanoparticles: From Plasmon-induced Chemistry to Photothermal Absorption***, A. Alvarez Barragan, C. Berrospe Rodriguez, **Lorenzo Mangolini**,* University of California, Riverside

The light-harvesting capacity of plasmonic nanoparticles has recently garnered attention in the synthesis of plasmon-driven photocatalysts. Gold and silver have been used to successfully drive hydrogen dissociation and CO oxidation reactions by injecting hot electrons into molecules adsorbed to their surface. However, the chemical instability of silver and the low thermal stability of both metals, in addition to their high cost, 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 visible-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 synthesis of TiN nanoparticles via a non-thermal plasma method. It also highlights the potential of this material as an alternative in plasmonic catalysis and as a high-temperature-resistant photothermal absorber. 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. Platinum nanoparticles were subsequently deposited on the TiN by photo-induced reduction of an aqueous solution of chlorplatinic acid (H_2PtCl_6). The reduction of the precursor metal was driven by electron hole pair generation via plasmon decay. The addition of methanol as a hole scavenger increased the electron lifetime, leading to the obtention of metallic platinum. This reaction occurred at temperatures below 40°C under visible light illumination. In addition, a novel $TiN@SiO_xN_y$ core-shell structure is facilitated by the modular capabilities of the non-thermal plasma synthesis method. The plasmon peak of the extinction spectrum of the core-shell particles is enhanced by 60% compared to the uncoated TiN particles. The high temperature resistance of these heterostructures is also demonstrated, as their optical properties remain stable at 700 °C under vacuum and at 400 °C in air. This work strengthens the case for alternative plasmonic materials in fields dominated by precious metals, and heavily driven by materials cost.

9:20am **PS+EM-WeM5 Plasma-induced Strain in MoS_2 Films for the Electrochemical Hydrogen Evolution Reaction***, T. Liu, X. Liu, **Souvik Bhattacharya**,* Case Western Reserve University*; Z. Ye, R. He,* Texas Tech University*; X.P.A. Gao, R. Akolkar, R.M. Sankaran,* Case Western Reserve University

There has been recent interest in growing layered materials such as molybdenum disulfide (MoS_2) over large areas for electronic and energy applications. One such approach is chemical vapor deposition (CVD) in which vapor precursors are thermally decomposed to nucleate a thin film at the surface of a substrate. A plasma may also be employed to assist in decomposition of the precursor molecule through gas-phase excitation, for example in plasma-enhanced CVD (PECVD) or plasma-enhanced atomic layer deposition (PEALD). Here, we report a plasma-assisted approach which is fundamentally different than these deposition techniques which we term plasma-enhanced chemical film conversion (PECFC). Precursor films are first prepared as a thin film on a substrate from liquids and subsequently converted by a combination of heating and plasma treatment. The process is additive, in that the precursor is only present where it is desired and there is little materials wastage, and substrate-independent, by circumventing the need for adsorption, allowing direct growth on application-specific substrates.

In this talk, we will present results for the synthesis of MoS_2 films and their application as electrocatalysts for the hydrogen evolution reaction (HER). A single-molecule precursor, ammonium tetrathiomolybdate (ATM), was first dispersed in solution with linear polyethylenimine (L-PEI) and spin-coated to produce a well-defined thin film less than 50 nm thick. The precursor film was then treated by an atmospheric-pressure dielectric barrier discharge (DBD) in a background of argon and hydrogen gas (80:20) at 500 ^oC. Conversion to crystalline MoS_2 was confirmed by X-ray diffraction and micro Raman spectroscopy. Atomic force microscopy was performed to study possible nucleation and growth mechanisms by varying the growth temperature and treatment time. The chemical composition was analyzed by X-ray photoelectron spectroscopy which showed an ideal stoichiometric ratio of 1:2 Mo:S.

A potential application of MoS_2 films is HER because it is composed of earth abundant elements and has been shown to be highly active through its edge sites. We carried out a systematic study of the origin of HER activity in our films, both after initial conversion and after several other post-synthesis treatments . The investigation showed that our initially-converted films have tensile strain leading to intrinsic activity that is comparable to previously reported sulfur vacancy generation by post-synthesis plasma treatment steps. In our case, the strain is induced in the initial fabrication step, providing a simpler and more scalable process to produce efficient HER electrocatalysts.

9:40am **PS+EM-WeM6 Comparison of Pulsed and Continuous Wave Argon Plasmas for the Synthesis of Vertical Graphene Nanosheets***, **Zoe Mann**, E.R. Fisher,* Colorado State University

Vertical graphene nanosheets (VGNs) have unique structural and electronic properties that make them applicable in fields such as energy storage, electronics, and sensing. VGNs are often grown using high-power, high-temperature processes and hazardous or unsustainable precursors such as methane. For this reason, we sought to develop a simple, efficient, and more environmentally-friendly way to synthesize VGNs. In this work, VGNs are synthesized from butter or coconut oil (sustainable, non-toxic precursors) spread on a Ni foam or Cu substrate and then treated with a high peak power pulsed plasma process. The materials formed through this process are compared to those produced with a continuous wave treatment of equivalent power and a low peak power pulsed plasma treatment, as well as to the untreated material. We used a range of characterization techniques to assess the materials, including scanning election microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and cyclic voltammetry, providing data on the morphology, surface chemistry, bulk characteristics, and electrochemical performance, respectively. SEM imaging shows that VGNs grown by the high power pulsed PECVD technique have high surface area and abundant ultra-thin edges. XPS analysis of untreated butter and the low-power pulsed plasma treated samples reveals binding environments consistent with the chemical composition of triglycerides (the primary chemical component in butter/oil), whereas the XPS and Raman spectra of VGNs indicate the presence of sp^2-hybridized carbon. Notably, cyclic voltammograms of VGNs formed on Ni foam are characteristic of a capacitor, and these materials do not exhibit the deleterious side reactions found with VGNs formed on the Cu substrate. To better understand the underlying chemistry occurring during plasma treatment, optical emission spectroscopy data were collected, revealing key information on species important for VGN synthesis, such as atomic and molecular carbon.

New Challenges to Reproducible Data and Analysis Focus Topic
Room A124-125 - Session RA+AS+CA+PS+TF-WeM
Reproducibility in Science and Engineering, Including Materials and Energy Systems

Moderators: Karen Gaskell, University of Maryland, College Park, Svitlana Pylypenko, Colorado School of Mines

8:00am **RA+AS+CA+PS+TF-WeM1 Reproducibility and Replicability in Science and Engineering: a Report by the National Academies***, **Dianne Chong**,* Boeing Research and Technology (Retired) **INVITED**

One of the pathways by which scientists confirm the validity of a new finding or discovery is by repeating the research that produced it. When a scientific effort fails to independently confirm the computations or results of a previous study, some argue that the observed inconsistency may be an important precursor to new discovery while others fear it may be a symptom of a lack of rigor in science. When a newly reported scientific study has far-reaching implications for science or a major, potential impact on the public, the question of its reliability takes on heightened importance. Concerns over reproducibility and replicability have been expressed in both scientific and popular media.

As these concerns increased in recent years, Congress directed the National Science Foundation to contract with the National Academies of Science, Engineering, and Medicine to undertake a study to assess reproducibility and replicability in scientific and engineering research and to provide findings and recommendations for improving rigor and transparency in research.

The committee appointed by the National Academies to carry out this task included individuals representing a wide range of expertise: methodology and statistics, philosophy of science, science communication, behavioral and social sciences, earth and life sciences, physical sciences, computational science, engineering, academic leadership, journal editors, and industry expertise in quality control. Individuals with expertise pertaining to reproducibility and replicability of research results across a variety of fields were included as well.

This presentation will discuss the committee's approach to the task and its findings, conclusions, and recommendations related to factors that influence reproducibility, sources of replicability, strategies for supporting reproducibility and replicability, and how reproducibility and replicability fit into the broader framework of scientific quality and rigor.

8:40am **RA+AS+CA+PS+TF-WeM3 Directly Assessing Reproducibility in Materials Chemistry Research Using Literature Meta-analysis***, **David Sholl**,* Georgia Institute of Technology **INVITED**

While it is widely agreed that making reported research more reproducible is a desirable goal, less is known about how reproducible current work in materials chemistry is. I will discuss using literature meta-analysis as a tool to obtain quantitative insight into the reproducibility of materials chemistry experiments. Case studies will be discussed involving measurements of gas adsorption in metal-organic frameworks and the synthesis of metal-organic framework materials. These are useful examples to study because comprehensive databases of information from the open literature are available, but they share features that are common in many areas of material chemistry. Insights from these case studies suggest possible paths towards improving data reproducibility for individual researchers, for academic departments and for professional organizations.

9:20am **RA+AS+CA+PS+TF-WeM5 Reproducibility in Fundamental and Applied Science***, **George Crabtree**,* Argonne National Laboratory, University of Illinois at Chicago **INVITED**

The scientific enterprise operates via a few basic features, including questions, insight, hypotheses, critique, reproducibility, elaboration and revision. All contribute to the process of discovery, none can be taken as the single signature of scientific truth. Discovery science is a dynamic process informed by new observations and continuous refinement of the precision, accuracy, principals and scope of our collective scientific knowledge. History has many examples of significant revisions of previously accepted dogma based on new observations (the earth is flat, matter is infinitely divisible, the stars are fixed). New insights lead to new fundamental principles (energy is conserved, nothing can go faster than light, germs cause disease) that open new opportunities for advancing the scientific frontier and raising the quality of life. Examples of advances of the frontiers of energy science and their implications for reproducibility will be given.

11:00am **RA+AS+CA+PS+TF-WeM10 Representativeness of a TEM image for Revealing New Phenomenon in Energy Storage Materials***, **Chongmin Wang**,* Pacific Norththwest National Laboratory*; D.R. Baer,* Pacific Northwest National Laboratory

Transmission electron microscopy (TEM), as a imaging technique with high spatial resolution, appears to be a routine tool for showcasing, often viewed as an enlightening figure, the structural and chemical information of materials at multiscale of down to single atomic column. One of a very common questions that raised by the viewer, not necessarily suspicious, is the representativeness of the image to the real situation as considering the sampling scale of the TEM imaging method. This question is further elevated for the case of in-situ and operando observation as which naturally couples in another dimension of “time” in addition to the “spatial” scale. In addition, beam effect can be coupled in for artifacts. In this presentation, we will check into the reproducibility of TEM imaging of both in-situ and ex-situ for revealing new phenomenon in energy storage materials, while certain cautions may also be necessary for interpreting new observations based on TEM.

11:20am **RA+AS+CA+PS+TF-WeM11 Reproducibility Issues when Developing Catalysts for Fuel Cell Applications***, M.J. Dzara, S.F. Zaccarine,* Colorado School of Mines*; K. Artyushkova,* Physical Electronics and University of New Mexico*; **Svitlana Pylypenko**,* Colorado School of Mines

This talk will discuss reproducibility issues encountered during the development of novel catalysts for low temperature fuel cell performance (PEMFC) as replacements of state-of-the-art catalysts that contain Pt-based nanoparticles supported on a high surface area carbon support. Examples across several catalytic systems will be shown, including low platinum-group metal (low-PGM) catalysts with extended surfaces derived from nanowire templates, and PGM-free catalysts based on N-doped carbon with an atomically dispersed transition metal.

Reproducibility issues related to the synthesis of these catalytic materials and their impact on the performance of these catalysts will be reported first following by discussion of challenges in characterization. Specifically, the need for complementary characterization will be highlighted along with issues that arise when materials are characterized by different groups using different techniques. Another set of reproducibility issues arises when conducting characterization of catalysts under in-situ and in-operando conditions.[1] The time constraints imposed by the availability of

instrumentation result in datasets that have a limited number of samples, areas per samples and replicate measurements on the same sample.

(1) Dzara, M. J.; Artyushkova, K.; Shulda, S.; Strand, M. B.; Ngo, C.; Crumlin, E. J.; Gennett, T.; Pylypenko, S. Characterization of Complex Interactions at the Gas − Solid Interface with in Situ Spectroscopy : The Case of Nitrogen-Functionalized Carbon. *J. Phys. Chem. C***2019**, *123* (14), 9074–9086.

11:40am **RA+AS+CA+PS+TF-WeM12 Challenges in Multimodal Spectroscopic Analysis of Energy Storage Materials***, **Vijayakumar Murugesan,*** Pacific Norththwest National Laboratory*; K.T. Mueller,* Joint Center for Energy Storage Research (JCESR) **INVITED**

Charge transfer across heterogeneous interfaces facilitated by redox reactions is the basis of energy storage technology. Capturing the interfacial processes over broad scales both spatially (ranging from angstroms up to 100 nm) and temporally (lasting from fs up to a few minutes) is a major challenge. This is one origin of the existing knowledge gaps in energy storage materials, which impede our ability to predict and control the emergent behaviors at electrochemical interfaces. As part of Joint Center for Energy Storage Research (JCESR) center, we developed a multi-modal in situ characterization tool set based on X-ray absorption, photoelectron and multinuclear NMR spectroscopy in combination with computational modelling that can access a range of the important complex processes. This multimodal approach helps us gain critical insights of the charge transfer process, but also presented unique challenges in data collection, analysis and reproducibility. The multitude of constituents and varying surface chemistry combined with external stimuli (applied potential and temperature) challenges the traditionally conceived time and spatial resolution limitations of the probes. For example, establishing reference systems and base line measurements for electrochemical process where combinatorial constituents react and depend on the charge state is a major challenge in spectroscopic studies and complicates subsequent corroboration with computational analysis. In this talk, we will discuss overcoming these challenges and apply the methods to critically analyzing solid-electrolyte interphase (SEI) evolution in Li-metal based batteries, multivalent ion transport across membranes and chemical stability of redox flow battery electrolytes.

Wednesday Afternoon, October 23, 2019

Plasma Science and Technology Division
Room B130 - Session PS-WeA

Commemorating the Career of John Coburn (ALL INVITED SESSION)

Moderators: David Graves, University of California at Berkeley, R. Mohan Sankaran, Case Western Reserve University

2:20pm **PS-WeA1 INVITED TALK: A Tribute to John W. Coburn*, David Graves,*** University of California at Berkeley

Dr. John W. Coburn was one of the most influential low temperature plasma and surface scientists of the 20th century. He passed away in San Jose, California on November 28, 2018. In this talk, I will summarize some of John's many contributions and his enormous impact on both fundamental understanding and applications associated with plasma-surface interactions, thin film deposition and etching. John was born in Vancouver, British Columbia and received his BS degree in Engineering Physics and his PhD in Electrical Engineering from the University of Minnesota. After his postdoctoral work at Simon Fraser University, John joined IBM Research (Almaden, California) in 1978. He worked at IBM for 25 years, and retired in 1993. John joined the AVS while still in graduate school and he served as the National AVS Treasurer for many years and in addition served as President in 1988. In 1994, John began to collaborate with me at UC Berkeley as a Senior Research Associate in the department of Chemical Engineering. He had a tremendous impact on me and my group over a period of over 20 years. This impact was both scientific and personal. In this talk, I describe some of John's most important work in non-equilibrium plasma science and plasma-surface interactions, with a special emphasis on the work he did at UC Berkeley with me and my co-workers.

2:40pm **PS-WeA2 INVITED TALK: Interfacial Chemistry in Highly Reactive Systems*, Frances Houle,*** Lawrence Berkeley National Laboratory

I joined IBM shortly after John Coburn and his close collaborator, Harold Winters, began publishing their seminal papers on use of XeF_2 to understand fundamental processes involved in plasma etching of silicon. They introduced me to the world of disordered surface reaction environments, and to the techniques they used to carry out careful experiments that shed light on how manufacturing processes work. I saw that it was possible to use well-chosen model systems to make sense of what controls interfacial chemistry in highly reactive, complex systems, and have been working on this type of problem ever since. In this talk I will describe how I have used model systems and multiscale computation to investigate the chemistry of oxidation of nanoscale organic aerosol by OH, relevant to atmospheric processes, and the photochemical generation of charge in porous photoanodes, relevant to solar energy conversion. In both cases, the interplay between transport and reactions is very sensitive to the composition of the chemical system, revealing opportunities for learning how to think more generally about rules governing interfacial reactivity.

3:00pm **PS-WeA3 INVITED TALK: Rare Gas Actinometry Turns Thirty Nine and is Still Finding Applications*, Vincent M. Donnelly,*** University of Houston

Ever since the first paper on rare gas actinometry (as it would later be called), published by Coburn and Chen, this method has been widely used to measure relative and sometimes absolute number densities of atoms and small molecules. The problem originally chosen by Coburn and Chen of measuring F atom densities with Ar as the rare gas turns out to be one of the most reliable applications of this diagnostic method, for an important etchant species that is difficult to detect by other techniques. The precision of F-atom actinometry can be attributed, first, to the (apparent) match between the relative energy dependence for the electron-impact excitation cross section of F 703.7 nm emission, compared with that for Ar $2p_1$ emission at 750.4 nm. Second, the large degree of dissociation for even moderate density plasmas with typical feed gases (CF_4/O_2, SF_6, NF_3, etc.), produces high F concentrations, so dissociative excitation of F emission from other F-containing species is usually negligible. This talk will briefly review actinometry as a plasma diagnostic with an emphasis on the issues related to its quantitative application, including cases where it can be used reliably, and others that should be interpreted with caution. Recent experiments that highlight the power of this technique will be discussed, including several studies relying on other work by John Coburn.

3:20pm **PS-WeA4 INVITED TALK: A Leader In Etching (ALE): How John Coburn Paved the way for Atomic Layer Etching*, Jane P. Chang,*** University of California, Los Angeles

This talk pays tributes to John Coburn's seminal contributions in the field of anisotropic etching by plasmas. John Coburn's early publication on "a system for determining the mass and energy of particles incident on a substrate in a planar diode sputtering system " set the tone for his many decades of research effort – deciphering the complex reaction mechanisms during plasma-surface interactions. Inspired by John Coburn's dedicated and outstanding contributions to the field of plasma processing, this talk highlights how the most recent development in anisotropic atomic layer etching can trace its root to John Coburn's work on delineating the reaction synergism between energetic ions and reactive neutrals. In John Coburn's words, "Today each wafer is exposed to a plasma etching environment between 10 and 20 times during its manufacture and without the highly anisotropic etching provided by this critical process, high density integrated circuit manufacturing would not be possible." This talk does not attempt to review all of John Coburn's work but focuses on the insight he provided to the research communitythat enabled the continued advances in the field where desirable etch specificity, selectivity, and anisotropy can be simultaneously achieved at the atomic scale.

4:20pm **PS-WeA7 INVITED TALK: Materials Processing Using Low Temperature Plasma Surface Interactions: Examples of the Influence of John Coburn*, Gottlieb S. Oehrlein,*** University of Maryland, College Park

John Coburn's pioneering work on plasma-assisted etching reactions of materials has had a profound and lasting influence on our scientific understanding and approaches of studying mechanisms of low temperature plasma-assisted processing of materials. As a colleague at IBM Research I had the opportunity to learn from and interact with John, and his colleagues Harold Winters and Eric Kay, with whom he worked very closely for many years. In this talk I will discuss several topics that were important to John, and how they reflected in my own research and recent work performed by members of my group, including ion bombardment, ion-neutral synergies and etching directionality in pattern transfer, the fluorine/carbon ratio of fluorocarbon etching chemistries introduced by John and colleagues, and several related topics.

4:40pm **PS-WeA8 INVITED TALK: A Brief Overview on Molecular Dynamics Simulations of Plasma-surface Interaction in Reactive Ion Etching*, Emilie Despiau-Pujo,*** LTM, Univ. Grenoble Alpes, CNRS, France

In the mid-70s, John Coburn and his colleague Harold Winter started to study plasma etching and reactive ion etching (RIE) processes which, at that time, were starting to be considered for pattern transfer and stripping processes in the semiconductor industry. Their research work focused on the physico-chemical mechanisms involved in this process, emphasizing surface science aspects, and continued for almost 20 years until they both retired from IBM in 1993. By designing insightful experiments, they highlighted in particular the role of energetic ion bombardment in RIE or the mechanisms responsible for a good Si/SiO_2 selectivity. 25 years later, reactive ion etching is a key process which has played a crucial role in the progress made in micro- and nano-electronics, a field which has affected every aspect of our modern lives.

Nowadays, advanced transistors feature ultrathin layered materials and must be etched with a nanometric precision and a nearly infinite selectivity to preserve the electronic properties of active layers. This challenge can no longer be addressed by conventional CW plasma processes, in which the ion-neutral synergy tends to create thick reactive layers which can compromise the etch precision. Alternative plasma technologies are thus needed and various approaches are investigated, to reduce the ion energy by decreasing the electron temperature (e.g. pulsed or low-Te plasmas), to avoid thick reactive layers using sequential and limited reaction steps (e.g. plasma-enhanced ALE), or to decouple the action of ions and radicals using sequential ion modification and chemical removal steps.

As shown by John Coburn during his entire career, the development of advanced etch processes requires a fundamental understanding of the surface reaction mechanisms involved in plasma-material interaction. Coupled with plasma diagnostics and surface characterization tools, Molecular Dynamics (MD) simulations can provide information about the reactions processes involved at the atomic scale and help to understand the phenomena governing the etch process. Since the pioneering work of Harrison et al. in the late 60s [1], atomistic simulations have been routinely used to study RIE and were shown to be a powerful tool to understand how the flux and energy of plasma species affect the structural and chemical modification of substrates. This talk will provide a brief overview of the

basics of molecular dynamics for RIE simulations (principles, accessible time and length scales, suitable force fields, etc.) as well as a review of various works performed on this topic from the 70s until very recently.

[1] D. E. Harrison et al, J. Appl. Phys. 39, 3742 (1968)

5:00pm **PS-WeA9 INVITED TALK: Plasma ALD – A Discussion of Mechanisms***, K. Arts, V. Vandalon,* Eindhoven University of Technology, The Netherlands, Netherlands*; H.C.M. Knoops,* Eindhoven University of Technology, The Netherlands*; **Erwin Kessels**,* Eindhoven University of Technology, The Netherlands, Netherlands

The profound contributions of John Coburn and Harold Winters to the field of plasma etching have inspired us at the Eindhoven University of Technology to study the mechanisms of plasma deposition [1]. In the last two decades our interest has mainly focused on the surface reactions during atomic layer deposition (ALD), especially on those during plasma-enhanced ALD (also referred to as plasma ALD or radical-enhanced ALD). In his late work, John Coburn has also worked on radical-enhanced ALD, more particularly on radical-enhanced ALD of TiN as investigated by fundamental beam studies [2]. As in his work on plasma etching, a lot of attention was given to the determination of sticking and reaction probabilities as quantitative knowledge of these parameters is key to gain a detailed understanding of the ruling reaction mechanisms. Moreover, quantitative information is needed for modelling purposes. In this contribution, some of our recent work on the determination of sticking and recombination probabilities during (plasma) ALD will be presented. Data obtained from broadband sum-frequency generation [3] and thin film conformality studies [4] will be reported and mechanisms underlying the ALD processes will be discussed.

[1] https://www.atomiclimits.com/2017/11/25/surface-science-aspects-of-plasma-ald-reactions-extending-the-legacy-of-harold-winters/

[2] F. Greer, D. Fraser, J.W. Coburn, and D.B. Graves, J. Vac. Sci. Technol. A 21, 96 (2003)

[3] V. Vandalon and W. M. M. Kessels, J. Vac. Sci. Technol. A 35, 05C313 (2017).

[4] K. Arts, V. Vandalon, R.L. Puurunen, M. Utriainen, F. Gao, W.M.M. Kessels, and H.C.M. Knoops, J. Vac. Sci. Technol. A 37, 030908 (2019)

5:20pm **PS-WeA10 INVITED TALK: RF Plasmas for Material Etching, Deposition, and Surface Modification***, **Dennis Hess**,* Georgia Institute of Technology

For the past 40 years, rf plasmas have been used extensively for thin film etching and deposition in electronic and photonic device fabrication. However, unique surface properties on materials such as paper and other porous substrates can be generated using these low temperature reactive atmospheres. Examples of surface modification for applications in paper-based medical tests strips and microfluidic device structures through the use of fluorinated and non-fluorinated plasma treatments will be presented.

Atomic Scale Processing Focus Topic
Room B130 - Session AP+PS+TF-ThM

Thermal Atomic Layer Etching

Moderators: Eric A. Joseph, IBM T.J. Watson Research Center, Harutyun Melikyan, Micron Technology

8:00am **AP+PS+TF-ThM1 A Challenge for Selective Atomic Layer Etching of Non-volatile Materials Using Organometalic Complex***, **Yoshihide Yamaguchi**, S. Fujisaki, K. Shinoda,* Hitachi, Japan*; H. Kobayashi, K. Kawamura, M. Izawa,* Hitachi High Technologies, Japan **INVITED**

Remarkable progress on atomic layer etching (ALE) for non-volatile materials has been made in recent years. The typical procedure for thermal ALE of non-volatile materials such as HfO_2 is cyclic repetitions of formation and desorption of the organometallic complex at a constant temperature [1]. The most significant problem in thermal ALE is formation of a volatile organometallic complex layer on the surface. The organometallic complex layer prevents diffusion of etching species into the deep at the formation step and must be easily removed at the desorption step. The thermal ALE of La_2O_3, however, is difficult to apply because the organo-lanthanum complexes are easily decomposed by mild heating (< 200 deg. C) and fail to prevent the diffusion. To solve this thermal instability, the authors have applied a thermal cycle ALE [2,3], which is a combination of a formation of the organo-lanthanum complex at a low temperature and a desorption of the complex at a high temperature. In this paper, several results of our challenge for thermal ALE of non-volatile materials using a selective organo-metallization reaction on the surface will be discussed. Some guiding principles for the organo-metallization reaction will also be explained.

A La_2O_3 thin-film sputtering deposited on a SiO_2/Si wafer was used as a sample. First, the La_2O_3 film was exposed to vapor mixture of a diketone and a stabilizer as the etchant gas at below 150 deg. C. Then the sample was annealed up to 250 deg. C. Temperature dependence in the procedure was also evaluated. After these consecutive processes, the sample was analyzed by scanning electron microscopy, X-ray photoelectron spectroscopy. Formation of the organo-lanthanum complex showed temperature dependent quasi-self-limiting characteristics. In the lower temperature range, the self-limiting characteristics enable precise control of the organo-lanthanum complex formation. In the higher temperature range, the continuous characteristics enable a higher etch amount per cycle with high selectivity. Several differences between chemistry with and without a stabilizer in the etching gas will be discussed. The high etching selectivity of La_2O_3 to HfO_2 was also demonstrated. From these findings, we conclude that practical ALE of La_2O_3 has been successfully demonstrated.

[1] Y. Lee et al., Journal of Vacuum Science & Technology A 36, 061504 (2018).

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

[3] Y. Yamaguchi et al., ALE workshop TuM4 (2018).

8:40am **AP+PS+TF-ThM3 Characterization of Isotropic Thermal ALE of Oxide Films and Nanometer-Size Structures***, **Andreas Fischer**, A. Routzahn, T.B. Lill,* Lam Research Corporation

In this work, we have characterized the reaction of aluminum oxide via the DMAC ligand exchange mechanism.

Fluorination studies of aluminum oxide were performed using NF_3, CF_4 or anhydrous HF, respectively. We also explored various methods of fluorination of the oxide surface such as thermal, in-situ or remote plasma, respectively, and found that a sufficient fluorine concentration could be obtained with either of the methods or reactants to enable atomic layer etching (ALE).

To understand reaction kinetics, we examined the interaction of aluminum fluoride (AlF_3) films with DMAC. We found that AlF_3 etched until it was completely consumed by DMAC. An analysis of its temperature-dependence allowed us to extract activation energies for the ligand exchange mechanism.

In a third part we demonstrated the utility of HF/DMAC reaction for isotropic ALE applied to nanometer-size metal oxide structures on wafers. Various metal oxides were etched and selectivities between oxides and potential mask materials were determined.

9:00am **AP+PS+TF-ThM4 Advanced Selective Chemical Dry Etch for Oxide and Si-based Material***, **Li-Hung Chen**, T. Kato, K. Nakahata, K. Takeya,* Tokyo Electron Technology Solutions Limited, Japan

As device features continuously shrink with introducing complex structures and new materials in semiconductor manufacturing, extremely high selectivity for etch processes have become more and more important. High selective chemical dry etch is developed utilizing a separated damage-free chemical removal chamber and sublimation chamber. The required selectivity is realized by using various chemistries and quantum mechanics analysis.

Firstly, HF/NH3 chemistry is used for oxide etch with high selectivity to SiN, Si, metals and resist. On the other hand, HF mono chemistry can etch SiN with high selectivity to oxide and Si. Quantum mechanics analysis revealed that NH_3 combined with HF enhances the SiO_2 reaction because of its lower activation energy. However, HF mono chemistry enhances the SiN reaction because of its lower activation energy than the oxide reaction[1)]. Secondly, Gas A chemistry is introduced for etching low quality oxide with selectivity >50 to both high quality oxide and SiN. The reaction rate barrier determined by quantum mechanics shows that etch reactivity with ALD-oxide is higher than with Th-SiO2 and SiN in Gas A etch process. Furthermore, Si and SiGe etch are evaluated with different Gas B/C ratio. Etch amount of Si is increased with increasing Gas C flow which can reduce activation energy from quantum mechanics simulation. Moreover, SiGe etching amount is decreased with increasing Gas C flow. This means that selectivity between Si and SiGe can be precisely controlled by Gas flow ratio.

Various applications can be realized by utilizing chemical dry etch with specific chemistries. For oxide etch processes such as fin recess, air gap, hard mask removal and surface clean, HF/NH3 chemistry can be used to meet critical criteria such as oxide selectivity to Si, SiN, resist and metal. CIP HW is developed to enhance throughput with excellent etch selectivity and uniformity. Additionally, HF mono-gas (or F-containing treatment) can dope Fluorine (F) into oxide film which is confirmed by depth profile analysis of secondary ion mass spectrometry (SIMS), and F implantation is known for dielectric breakdown life time improvement[2)]. Also, Gas A can be utilized in Silica oxide removal process, which requires high selectivity between low quality and high quality oxide. Finally, Si mandrel removal and Si or SiGe nanowire fabrication is introduced by controlling gas flow ratio. Further discussion will be presented on AVS 66th.

Reference

[1] T. Kato, et al., AVS 65th Int. Symp. & Exhibit. (2018)

[2] Y. Mitani, et al., Proc. Of IEEE P93-98 (1999)

9:20am **AP+PS+TF-ThM5 Mechanisms of Thermal Atomic Layer Etching (ALE) of Metal by Deprotonation and Complex Formation of Hexafluoroacetylacetone (hfacH)***, **Abdulrahman Basher**[1], I. Hamada,* Osaka University, Japan*; M. Krstic,* Karlsruhe Institute of Technology (KIT), Germany*; M. Isobe, T. Ito,* Osaka University, Japan*; K. Fink,* Karlsruhe Institute of Technology (KIT), Germany*; K. Karahashi, Y. Morikawa,* Osaka University, Japan*; W. Wenzel,* Karlsruhe Institute of Technology (KIT), Germany*; S. Hamaguchi,* Osaka University, Japan

Thermal atomic layer etching (ALE) may be used for precise and damageless etching of difficult-to-etch materials such as Ni, Co, NiFe, MgO, and CoFeB, which can be used as materials for magnetic tunnel junction (MTJ) stacks of magnetic random access memory (MRAM) devices. The goal of this study is to understand the mechanisms of surface chemical reactions during thermal ALE of metal in general with oxidation and exposure to organic molecules. As a model case, we consider a two-step thermal ALE process of nickel (Ni) with an oxidation step and a gas exposure step at an elevated substrate temperature [1]. In the latter step, hexafluoroacetylacetone (hfacH) $CF_3C(OH)=CHC(O)CF_3$ is used as a reactive gas. In the oxidation step, a thin layer of NiO is formed on the Ni film surface and, in the gas exposure step, only (part of) this NiO layer is removed and thus self-limiting etching of Ni is achieved. Our main question is why NiO is etched but Ni is not etched by hfacH. This mechanism is studied with first-principle simulation of interaction of hfacH with Ni and NiO surfaces.

First, we examined interaction of hfacH with a metallic Ni surface, using a simulation code STATE [2,3], which is based on density functional theory (DFT) with pseudo-potentials and a plane wave basis set. Computationally, a metal surface is better represented by a plane wave basis set in general.

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

It has been found in our simulation that, as an hfacH molecule approaches a metallic Ni surface with thermal velocity, it is more likely to be decompose and fragmented, rather than forming a hexafluoroacetylacetonate anion (hfac-) by deprotonation. This is consistent with earlier experimental observations [1,4]. The simulation clearly shows an energy threshold for deprotonation of hfacH with a metallic Ni surface.

Second, we examined interaction of enol hfacH with a NiO surface using a simulation code Turbomole [5], which is based on DFT but with Gaussian type orbitals. To better represent a NiO surface, we used the embedded cluster method (ECM) with Turbomole. It has been found that, as an hfacH molecule approaches a NiO surface, it is likely to deprotonate by transferring its hydrogen ion (H+) to an O atom of the NiO surface and the resulting hfac- tends to bond with a Ni atom of the surface because of the highly ionic nature of NiO, where Ni and O atoms are positively and negatively charged, respectively. In this way, volatile $Ni(hfac)_2$ and H_2O can be formed when hfacH molecules interact with a NiO surface. Reaction energies of such interactions have been evaluated from the simulations.

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[1] T. Ito, et al., AVS 65th International Symposium & Exhibition (2018).

[2] Y. Morikawa, H. Ishii and K. Seki, Phys. Rev. B, **69**, 041403 (2004).

[3] I. Hamada, Physical Rev. B **89**, 121103 (2014).

[4] H. L. Nigg and R. I. Masel, J. Vac. Sci. Techol. A **17**,3477 (1999).

[5] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Lett. **162**, 165 (1989).

9:40am **AP+PS+TF-ThM6 Thermal Atomic Layer Etching of Amorphous and Crystalline Al_2O_3 Films***, **Jessica A. Murdzek**, S.M. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) can be achieved with sequential, self-limiting surface reactions. One mechanism for thermal ALE is based on fluorination and ligand-exchange reactions. For metal oxide ALE, fluorination converts the metal oxide to a metal fluoride. The ligand-exchange reaction then removes the metal fluoride by forming volatile products. Previous studies have demonstrated the thermal ALE of amorphous Al_2O_3 films. However, no previous investigations have explored the differences between the thermal ALE of amorphous and crystalline Al_2O_3 films.

This study explored the thermal ALE of amorphous and crystalline Al_2O_3 films. HF or XeF_2 was used as the fluorination reactant. Dimethylaluminum chloride (DMAC) or trimethylaluminum (TMA) was employed as the metal precursor for ligand-exchange. The amorphous Al_2O_3 films had a much higher etch rate per cycle than the crystalline Al_2O_3 films. When using HF and TMA at 300 °C, the amorphous Al_2O_3 was removed at 0.78 Å/cycle, whereas the crystalline Al_2O_3 showed no significant thickness removal after 250 cycles (See Supplemental Figure 1). When using XeF_2 and TMA at 300 °C, the etch rate was 0.66 Å/cycle for the amorphous Al_2O_3 film. In comparison, ALE only removed up to 10 Å of the crystalline Al_2O_3 film. XeF_2 may be able to fluorinate the near surface region of the crystalline Al_2O_3 film easier than the crystalline bulk of the film.

The differences between amorphous and crystalline Al_2O_3 are sufficient to obtain selective thermal ALE of amorphous Al_2O_3 in the presence of crystalline Al_2O_3. The investigations also examined the effect of annealing temperature on the etch rate per cycle. Amorphous Al_2O_3 was etched at approximately the same etch rate until the crystallization of amorphous Al_2O_3 at >880 °C. The thermal ALE of crystalline films is important because amorphous films may not crystallize easily when they are too thin. Consequently, amorphous films may have to be grown thicker, crystallized, and then etched back to obtain the desired ultrathin crystalline film thickness.

11:00am **AP+PS+TF-ThM10 Thermal Atomic Layer Etching (ALE) of Germanium-Rich SiGe Films***, **Aziz Abdulagatov**, S.M. George,* University of Colorado at Boulder

The thermal atomic layer etching (ALE) of germanium-rich SiGe was demonstrated using an oxidation and "conversion-etch" mechanism (See Supplemental Figure 1). In this process, the SiGe surface was oxidized to a SiGe oxide layer using O_2. The SiGe oxide layer was then converted to an Al_2O_3 layer using trimethylaluminum (TMA). The Al_2O_3 layer was fluorinated by HF to an AlF_3 layer prior to the removal of the AlF_3 layer by ligand-exchange using TMA. The thermal ALE of SiGe films will be important for the fabrication of advanced MOSFET devices.

This study explored the thermal ALE of germanium-rich $Si_{0.2}Ge_{0.8}$ films. *In situ* spectroscopic ellipsometry was employed to monitor the thickness of both the $Si_{0.2}Ge_{0.8}$ and the surface oxide layer during ALE. These studies showed that the $Si_{0.2}Ge_{0.8}$ film thickness decreased linearly with number of reaction cycles while the surface oxide thickness remained constant. Using an O_2-HF-TMA reaction sequence, the $Si_{0.2}Ge_{0.8}$ ALE etch rate was 0.57 Å/cycle at 290°C. This etch rate was obtained using optimal reactant pressures of 25, 0.2 and 0.4 Torr, and dose times of 1.5, 1 and 1 s, for O_2, HF and TMA, respectively.

The $Si_{0.2}Ge_{0.8}$ ALE etch rate was lower at lower temperatures. Using an O_2-HF-TMA reaction sequence, the $Si_{0.2}Ge_{0.8}$ etch rate was reduced from 0.57 Å/cycle at 290°C to 0.07 Å/cycle at 225°C. The order of the reactant sequence also affected the $Si_{0.2}Ge_{0.8}$ etch rate. Changing the reactant sequence from O_2-HF-TMA to O_2-TMA-HF reduced the $Si_{0.2}Ge_{0.8}$ etch rate from 0.57 to 0.45 Å/cycle at 290°C. $Si_{0.2}Ge_{0.8}$ could also be etched selectively in the presence of Si and Si_3N_4. The $Si_{0.2}Ge_{0.8}$ etch rate was >10 times faster than the etch rate for Si or Si_3N_4 at 290°C (See Supplemental Figure 2).

11:20am **AP+PS+TF-ThM11 Thermal Atomic Layer Etching of GaN and Ga_2O_3 Using Sequential Fluorination and Ligand-Exchange Reactions***, **Nicholas Johnson**, Y. Lee, S.M. George,* University of Colorado at Boulder

Atomic layer etching (ALE) of GaN and Ga_2O_3 is important for the fabrication of power electronics devices. Thermal ALE of GaN and Ga_2O_3 was performed using sequential, self-limiting surface reactions. The thermal ALE was accomplished using fluorination and ligand-exchange reactions. XeF_2 and HF were used as the fluorination reactants. BCl_3 was the main metal precursor for ligand-exchange. Ga_2O_3 was also etched using $Al(CH_3)_3$, $AlCl(CH_3)_2$, $TiCl_4$ or $Ga(N(CH_3)_2)_3$ as the metal precursors for ligand-exchange.

Crystalline GaN samples prepared using MOCVD techniques at the US Naval Research Laboratory were etched with sequential XeF_2 and BCl_3 exposures. GaN etch rates varied from 0.18 to 0.72 Å/cycle at temperatures from 170 to 300°C, respectively (see Supplemental Figure 1). Because the GaN etch rates were self-limiting versus BCl_3 exposure and BCl_3 pressure, the GaN etching mechanism is believed to involve XeF_2 fluorination of GaN to GaF_3 and then ligand-exchange between BCl_3 and GaF_3 to yield volatile BCl_wF_x and GaF_yCl_z species. GaN fluorination using a NF_3 plasma was also successful for etching crystalline GaN at 250°C.

Ga_2O_3 samples deposited using ALD techniques were etched with sequential HF and BCl_3 exposures. Ga_2O_3 etch rates varied from 0.59 to 1.35 Å/cycle at temperatures from 150 to 200°C, respectively. The Ga_2O_3 etch rates were self-limiting versus HF and BCl_3 exposure. Ga_2O_3 ALE was also performed using HF for fluorination and a variety of metal precursors for ligand-exchange. Ga_2O_3 etch rates at 250°C were 0.2, 0.8, 1.1 and 1.2 Å/cycle for $Ga(N(CH_3)_2)_3$, $TiCl_4$, $Al(CH_3)_3$ and $AlCl(CH_3)_2$ as the metal precursors, respectively (see Supplemental Figure 2). The wide range of metal precursors that can etch Ga_2O_3 argues that the ligand-exchange reaction with GaF_3 is facile.

11:40am **AP+PS+TF-ThM12 Mechanistic Insights into Thermal Dry Atomic Layer Processing of Metals***, **Andrew Teplyakov**,* University of Delaware **INVITED**

The mechanisms of thermally induced reactions of atomic layer deposition (ALD) and atomic layer etching (ALE) can be sometimes viewed as proceeding in opposite directions. However, for atomic layer processing of metals, that would mean that the best designed and most efficient reaction pathways leading to metal deposition would produce insurmountable energy barriers for a reverse process. If ligand detachment, exchange, and decomposition could be desirable for ALD, the etching of the same metals would require careful consideration of the etching mechanisms at the atomic and molecular level. Given that the mechanisms of ALE can be very complex, the key concepts and approaches will be described here for thermal dry etching processing, which would allow for eliminating the role of solvents and for distinguishing thermodynamic and kinetic regimes of etching. The mechanistic investigation of thermal dry etching of cobalt will be the primary target of this work. This process will be used to illustrate the limitations of the single-reagent etching by analyzing the reaction of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone, hfacH) or 2,4-pentanedione (acetylacetone, acacH)) with a clean cobalt surface. Then the effects of surface oxidation and chlorination will be explored as a means of kinetically controlled process. Finally, a number of potential effects of the mechanisms of dry etching on the morphology of the surfaces produced and, specifically, on the "smoothing" effect of dry etching will be discussed.

Plasma Science and Technology Division
Room B131 - Session PS-ThM

Plasma Diagnostics and Sources II

Moderators: Geun Young Yeom, Sungkyunkwan University, Republic of Korea, Wei Tan, Applied Materials

8:00am **PS-ThM1 Measurement of Plasma Neutral Densities in a Very High Frequency Ar/NH_3 Plasma with a Line-of-sight Threshold Ionization Mass Spectrometry**, ***Jianping Zhao***, *P.L.G. Ventzek, C. Schlechte, M. Burtner,* Tokyo Electron America, Inc.*; D. Li, J.G. Ekerdt,* The University of Texas at Austin*; T. Iwao, K. Ishibashi,* Tokyo Electron Technology Solutions Limited, Japan

Atomic precision plasma processes for logic and memory fabrication are in increasing demand due to the shrink of critical dimensions to near physical limits and increase in stack complexity. Meeting dimensionality requirements is not enough. Infinite selectivity and damage-free process with sub-angstrom control are sought to deliver high quality films with productivity worthy yields. Plasma enhanced processes, particularly plasma enhanced atomic layer deposition (ALD) rely on plasma generated radicals for much of their perceived benefit. Furthermore, low energy ions are required to mitigate damage. Large-area plasma processing systems capacitively driven at very high frequencies (VHF, e.g. 100MHz) have attracted much interest for semiconductor device and flat panel display processing. VHF has the advantage of generating plasma with more efficiency as power is coupled more into electrons and less into ions in the sheath. Depending on the film and process, benefits are reduced ion energy and high radical and ion fluxes. It remains the case that it is difficult to relate the role of the combination of species flux and energy exactly to film growth mechanisms or material properties. Ideally, both species flux and film properties would be measured simultaneously (and in real time) as the surface state from ALD is changing continuously. A significant challenge is that it is difficult to measure the absolute density of neutral species in industrially relevant plasmas reliably especially at high pressure. In order to understand the fundamental plasma chemistry property of VHF plasma, we present here the measurement of the neutral species with a line-of-sight threshold ionization mass spectrometry (LS-TIMS) technology in VHF Ar/NH_3 plasmas. Ar/NH_3 plasma has been widely used in plasma enhanced ALD and CVD. Systematic measurements were performed in a 100 MHz plasma source with a wide RF power, pressure, Ar to NH_3 flow ratio range. Plasma chemistry properties of Ar/NH_3 plasma are derived after a careful background subtraction and mass-to-charge ratio dependent sensitivity calibration. Density of NH_3 and various amine dissociation products are determined as a function of plasma discharge conditions. The LS-TIMS results are also compared to those from other optical based neutral diagnostics.

8:20am **PS-ThM2 Radical Probe System for In-Situ Measurements of Hydrogen, Oxygen and Nitrogen Radical Densities**, ***Dren Qerimi***, *G.A. Panici, A.J. Jain,* University of Illinois at Urbana-Champaign*; J.W. Wagner,* Colorado State University*; D.N. Ruzic,* University of Illinois at Urbana-Champaign

The current state-of-the-art methods to identify presence of radical species in vacuum chambers are optical methods, which suffer from the lack of spatial resolution and require expensive optical equipment. Center for Plasma Material Interactions (CPMI) at the University of Illinois developed a catalytic radical probe array to measure concentrations of reactive species in low temperature plasma with high spatial resolution. Radical probes as plasma diagnostic tool can be used to determine radical densities of hydrogen, nitrogen and oxygen in any continuous plasma source in vacuum environment. The basic principle and advantage of a probe array is the capability to distinguish between different gas species due to several sensitive elements acting as recombination catalysts [1]. The catalytic coatings cover an area of several square millimeters on the tip of a sheathed thermocouple. The catalytic probe surface provides efficient recombination of active species with subsequent energy release as a heat. All the probes are exposed to the same background plasma heating/cooling mechanisms, but the temperatures are not the same due to the fact that different catalytic materials have different recombination coefficients, therefore a temperature difference between probes is generated. The system consists of two additional probes, first to obtain the overall heat flux on probe array, and the second is a reference probe with surface chemically active to all gases.

Lifetime of radical probes, specifically catalytic surface degradation, depends highly on vacuum conditions, chamber contamination and the fact that radical species cause surface properties to change. Lifetime of radical probe system is usually three hours. However, probe surface cleaning has been achieved by applying a bias which causes contamination layer on the probe tip to sputter via ion bombardment. Argon gas is used to sputter clean probe tip. Additionally, if probe shows signs of high contamination then a long sputtering process is used to remove all the catalytic material from the probe tip and then magnetron sputtering is used to redeposit new catalytic coating. The array of several probes is capable to distinguish between different gas species with sub centimeter spatial resolution. The probes give accurate results in a broad range of reactive species concentrations from about 10^{12} to 10^{14} cm^{-3}.

Reference:

[1] M Mozetic, M Kveder, M Drobnic, A Paulin, and A Zalar. Determination of atomic

hydrogen density with catalytic probes. Vacuum, 45(10-11):1095-1097, 1994.

8:40am **PS-ThM3 Post Charge Separation Grid Ion Flux Evaluation in Inductive Coupled Plasma Source Downstream Asher**, ***Luke Zhang***, *S. Ma,* Mattson Technology, Inc.

With semiconductor device shrink and gate dielectric thickness decrease, the potential for device damage at the photoresist strip level increase. It is desired to develop the downstream plasma asher producing high active radical concentration with low ion concentration while still maintaining excellent ash rate for different strip application. Therefore, it is critical to understand the population of charge species that can reach the wafer surface. In this study, an inductive coupled plasma (ICP) source with patented grounded Faraday shields is used [1], which offers superior resist strip capability to leading edge memory, logic and foundry applications. Faraday shield is used to reduce ion energy and electron temperature from plasma generation to obtain the better plasma damage performance. To further reduce the ion concentration on the wafer surface, charge separation conductive grid [2] is also added between the top plasma source and heated pedestal. By optimizing grid pattern, uniform gas and radical distribution can be obtained, thus the wafer uniformity can be improved. Ion flux underneath the grid are evaluated with different diagnostic tools to evaluate the grids effect including Langmuir probe and Retarding Field Energy Analyzer. The Langmuir probe with plasma detect limit 10^8 cm-3 is inserted plasma at 1cm above the pedestal is used to detect the ion flux underneath the grids. RFEA (Retarding Field Energy Analyzer) is equipped on the pedestal, which measures ion energy and ion flux directly. Both the diagnostics tools show that ion density is below the detection limit after charge separation grid. To further characterize the grid effect, one self-made thick probe with length 10mm and diameter 3.8mm inserted to the plasma with biased at negative voltage to measure ion saturation current, Pico amp accuracy ammeter is used to measure the collected current. It is found that grid dramatically reduce the ion saturation current, one thousandth of ion saturation current at Oxygen plasma detected under double grids compared to no grid condition. Different plasma chemistry and different grid are also evaluated.

[1] Stephen E. Savas, Brad S. Mattson, Martin L. Hammond, Steven C. Selbrede, Patent US 6143129

[2] Stephen E. Savas, Brad S. Mattson, Patent US 5811022

9:00am **PS-ThM4 Development of a Novel Langmuir Probe for the Investigation of Dusty Non-thermal Plasmas**, ***Austin Woodard***[1], *L. Mangolini, K. Shojaei, C. Berrospe,* University of California, Riverside

Dusty plasmas are characterized as plasmas containing micro- to nano-sized particles. Probing the plasma physics inherent in these systems is a daunting, but critical, task necessary for the engineering design and optimization of many common-place industrial manufacturing processes utilizing plasma, such as thin film etching and fabrication. We present the development of a test-bed for the characterization of dusty plasmas via a simple Langmuir probe. This diagnostic tool allows for the precise determination of the electron energy distribution function (EEDF) and subsequent plasma parameters but is notoriously difficult to use in dust-forming chemistries due to the inevitability of an insulating coating. To combat this, we have designed a two-stage reactor scheme that overcomes this limitation. In the first plasma reactor, the particle production cell, we synthesize graphitic carbon nanoparticles from the complete dissociation of acetylene, confirmed by a residual gas analyzer, which are then directly injected into the primary chamber volume. The quality of the measurement

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

is minimally affected by the presence of a graphitic nanoparticle coating on the probe tip due to its high electrical conductivity, thus creating a more forgiving environment in which to employ this technique. Additionally, the approach has the advantage of decoupling the nucleation and growth-phase kinetics of the nanoparticles from the primary chamber discharge thus allowing us to study the plasma properties when varying processing parameters such as primary plasma power and chamber pressure. Due to the particle trapping induced in the primary plasma, a continues wave laser (532 nm) was used to investigate the actual particle density in the primary chamber volume, and from this, the average charge per particle. The analysis of the EEDF as a function of the plasma parameters highlights the onset of unexpected trends in plasma the properties which are not predicted by traditional OML theory; we observe secondary peaks in the EEDF that change with the processing parameters, indicating not an electronic transition, but a phenomenon directly related to the presence of dust. To investigate this theoretically, we performed simulations with a Boltzmann-solver modified to account for the effect of secondary electron emissions. These simulations also exhibited a secondary peak, at the same energy levels observed experimentally; thus, we tentatively attribute this observation to secondary emission processes directly tied to the floating potential of the particles.

9:20am **PS-ThM5 Historical Review of Microwave Plasma Diagnostics using Plasma Cutoff Phenomenon**, ***Shin-Jae You***, *S.J. Kim,* Chungnam National University, Republic of Korea; *Dw. Kim,* KIMM, Republic of Korea **INVITED**

Though this paper, we present historial review of our cutoff probe research which has been performed for almost 2 decade. This paper focus on the whole progress for the cutoff probe including how to start to develop the cutoff probe in the initial period, what idea has been included during the development, how to evolve the probe during 17 years. The cutoff probe is most simple diagnostics among the plasma diagnostics tools which was made by simple intuition for the cutoff phenomenon of the plasma wave. However, the cutoff probe has been used for a long time without test of validation of probe itself. Later, EM waver simulation supported the validation for the cutoff frequency determination. Recently, by supposing the circuit modeling, the physics behind for the cut off probe spectrum (S21) was revealed and the accuracy and the application window of the probe were established. Very recently, as an extended version of the circuit model, we makes transmission line modeling to explain the cutoff spectrum in high density plasma as well as low density plasma.

Based on recent developments we also introduce a novel methodology to interpret the probe spectrum that eliminates the sheath and collisional effects and enables the use of this precise diagnostic technique in a broad range of practical processing conditions.

11:00am **PS-ThM10 Characterization of Inductive Coupled Plasma Source RF Power Pulsing for Advanced Surface Treatment Applications**, ***Shawming Ma***, *L. Zhang, D. Kohl,* Mattson Technology, Inc.

As device dimensions continue to shrink into the sub-10 nm regime, low electron temperature plasma and radicle energy control become very important factors in the fabrication of microelectronics device. A pulsing plasma reactor [1] is an efficient way to bring down the electron temperature and improve the process window by adding an additional tuning knob. Pulsed plasmas have been widely used in plasma etch tools, as high-density plasmas at low pressure demonstrate excellent plasma charge damage reduction, improved microloading and reduced mask erosion compared to traditional etchers. However, no results have thus far been reported for a high pressure, downstream pulsed plasma reactor for surface treatment and plasma ashing. For advanced surface treatment applications, radical energy control becomes necessary to control either selectivity to underlying films during resist ashing, surface film growth or surface property change. Therefore, it is desired to have radical energy control capability to improve the process window.

In this work, we explore pulsing plasma in a high pressure, downstream, grounded Faraday Shielded ICP source[2]. Source RF power of 13.56MHz frequency with pulsing frequency up to 100kHz and a vacuum capacitor automatch were used in the experiment. The pulsing window was mapped with maximum pulsing frequency 30KHz and duty cycle from 10% to 90%. A Langmuir probe is used to measure the electron energy distribution function (EEDF) developed by Plasma Sensor [3], which is inserted in the reactor 1cm above the wafer pedestal. Due to the limitations of plasma density measurement, (Langmuir probe requires plasma density above 10^8 cm-3 detection limit) the grid [4] which is used to separate high density and low density plasma, is removed from the reactor to make the measurement possible. Pulsed plasma program performs time resolved measurements of the probe V-I, the plasma parameters and EEDF. Both electropositive (e.g. Ar) and electronegative (O2/N2) plasma are used to study the pulsing plasma. The plasma impedance for the different plasma are read from the matching networks internal I-V probe. Electron temperature, density and afterglow temporal evolution at different pulsing conditions are also discussed.

[1] Pulsed plasma etching for semiconductor manufacturing, Demetre J Economou, J. Phys. D Appl. Phy. 47(2014)

[2] Stephen E. Savas, Brad S. Mattson, Martin L. Hammond, Steven C. Selbrede, Patent US 6143129

[3] Comparative analyses of plasma diagnostics techniques, V. A. Godyak and B. M. Alexandrovich, Journal of Applied Physics 118, 23302 (2015)

[4] Stephen E. Savas, Brad S. Mattson, Patent US 5811022

11:20am **PS-ThM11 In-situ Measurement of Deposited Tilm Thickness and Electron Density by Double Curling Probe**, ***Daisuke Ogawa,*** Chubu University, Japan; *Y. Sakiyama,* Lam Research Corporation; *K. Nakamura,* Chubu University, Japan; *H. Sugai,* Nagoya Industrial Science Research Institute, Japan

We developed a technique for measuring the thickness of a deposited film and electron density of a processing plasma simultaneously during a process with the use of two curling probes (CPs). As might be already known, CP is one of the microwave resonators which has a spiral-shaped slot antenna to make resonance. The resonance frequency (RF) depends on the geometry of the probe (the length and diameter of the antenna) and material of the antenna cover, etc., and the RF shifts to a higher frequency as electron density increases. Also, our recent research showed that CP can find the thickness of the film deposited after a plasma processing through the observed shift of RF when a dielectric constant of the film is known. In a deposition process operated in semiconductor industries, a film deposits not only on the processing substrate but also on a CP. The deposition shifts the RF lower, but the plasma shifts the RF higher. As a result, the observed shift in RF corresponds to a summation of the two shifts. This summation makes it difficult for us to discriminate the two shifts, but a pair of different-sized CPs (*double CP*) enables discrimination of the two shifts caused in the same plasma with the identical film thickness. We so far derived the equation giving the two shifts based on the previous theory. In order to confirm the solution of the equation, we performed a simple model experiment of deposition in an argon plasma, inserting two CPs covered with a polyimide film of known thickness (55-micrometer). We first measured the original RFs of the two probes with no polyimide film and no plasma exposure. And then, we measured the RF of each CP with a layer of the polyimide film and with plasma exposure. Finally, we derived the film thickness and electron density from the four RFs: the result revealed almost the same film thickness as the 55-micrometer polyimide film and the electron density of 2×10 cm^{-3} which decently matches with the Langmuir probe data. In this presentation, we will show our latest results using the double CPs with the industrial application in mind.

11:40am **PS-ThM12 Study of Selective PECVD of Silicon on Silicon Nitride and Aluminum Oxide**, ***Ghewa Akiki,*** *E.V. Johnson, P. Bulkin,* LPICM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, France; *D. Daineka,* LPICM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris

Research in the field of area selective deposition currently focuses on the use of Atomic Layer Deposition (ALD) technique, and requires an initial nucleation delay between two different substrates, as well as a "passivation" step, namely a plasma etching step that resets the nucleation delay for one surface [1]. In analogy, we aim to demonstrate a Plasma Enhanced Chemical Vapor Deposition (PECVD) based approach using a non-sinusoidal voltage waveform [2] to excite an $Ar/SiF_4/H_2$ plasma. This plasma chemistry is believed to be a key ingredient to creating a varying nucleation delay as the surface processes depend on the deposition/etching balance controlled by the H_2 flow rate [3]. As a building block for our PECVD based approach, we report on the observation of a nucleation delay for a PECVD process for microcrystalline silicon films on two different substrates, first using a standard 13.56 MHz radio frequency excitation source. The deposition selectivity on a patterned chip containing both SiN_x and AlO_x areas as well as the influence of the plasma parameters, will be presented. The analysis is performed by comparing ex-situ ellipsometry spectra before and after deposition and by Scanning Electron Microscopy (SEM) micrographs.

[1] R. Vallat, R. Gassilloud, B. Eychenne, and C. Vallée, **J. Vac. Sci. Technol. A 35,** 01B104 (2017)

[2] J. Wang and E.V. Johnson, **Plasma Sources Sci. Technol. 26** (2017) 01LT01

[3] Dornstetter JC, Bruneau B, Bulkin P, Johnson EV, Roca i Cabarrocas P, **J. Chem. Phys. 140**, 234706 (2014).

Advanced Surface Engineering Division
Room A215 - Session SE+PS-ThM

Plasma-assisted Surface Modification and Deposition Processes

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

8:00am **SE+PS-ThM1 Core/Shell Particles using a Plasma-based Reactors*, Santiago Vargas-Giraldo,* *D. Galeano-Osorio, C. Castano,* Virginia Commonwealth University

Nano-size and micro-size manufacturing have found an invaluable tool in plasma-assisted materials deposition techniques. Primarily, plasma-assisted physical vapor deposition (PAPVD) methods are clean, reliable and flexible to develop films and coatings. Materials produced by PAPVD may lead to stable structures and stoichiometries that are not possible on other processes. On the other hand, core/shell systems have dragged high attention due to their unique properties. These structures exhibit high surface area, and the interfacial interaction between the core and the shell leads to complex chemistries and transfer phenomena. This work presents an innovative approach to synthesize shells for existing particles using sputtering equipment. It demonstrates the challenges for the direct implementation of magnetron sputtering to obtain single and double shells on glass microspheres. First, a simple flat sample stage was used to discuss the prominent structural and conformability imperfections due to shadowing effects on 3D cores. To overcome this limitation, a new sample stage to manipulate the core particles under vacuum for more uniform shell formation was designed. As proof of concept, various metals and metal oxide shells over glass micro-size spheres were obtained. Extensive materials characterization of the newly formed structures was performed. The results are the groundwork for a myriad of technological applications.

8:20am **SE+PS-ThM2 Formation Mechanisms of Converted Layer During Erosion of Composite Al-Cr Arc Cathodes*, Mehran Golizadeh,*** *F. Mendez Martin, B. Rashkova,* Montanuniversität Leoben, Austria*; S. Kolozsvári,* Plansee Composite Materials GmbH, Lechbruck am See, Germany*; R. Franz,* Montanuniversität Leoben, Austria

Cathodic arc deposition (CAD) is a well-established physical vapor deposition technique which is characterized by a highly ionized plasma emitted from the cathode. The energy of the ions in the plasma ranges from 20 to some 100 eV, depending on the cathode material and the discharge conditions. These energetic and highly ionized plasmas significantly influence film growth mechanism and, e.g., high-temperature phases can be stabilized at typically low deposition temperatures in CAD. The plasma properties are influenced by the properties of the converted layer which forms on the surface of composite cathodes due to local consecutive melting-solidification cycles caused by the motion of the cathode spot over the cathode surface. Therefore, a detailed understanding of the formation mechanism and properties of the converted layer is essential to understand and manipulate plasma properties.

Within the current work, composite cathodes with composition of $Al_{0.5}Cr_{0.5}$ but different grain size, namely 80 and 1200 µm, were eroded in inert Ar gas at a pressure of 1 Pa applying a current of 60 A. A short erosion time of 30 s enabled us to capture single craters left behind by a cathode spot. A cross-section of the crater prepared using focused ion beam (FIB) showed the liquid pool formed by the cathode spot was violently deformed by plasma pressure, pushing the liquid out of the crater to the rim and surrounding space (macroparticles). The leftover liquid was rapidly quenched and there was almost no heat-affected zone below the crater. This finding shows that solid-state diffusion plays a negligible rule in the formation of the converted layer.

Further, cross-sections of the cathodes eroded for 1h were prepared by conventional metallography and FIB. Detailed microstructural and phase analysis using transmission electron microscopy and transmission Kikuchi diffraction together with cross-sectional study of single craters revealed that the converted layer is formed in a way that the rim of a crater fills the neighbouring craters due to step erosion. The splashes ejected from craters by plasma pressure also contribute to forming the converted layer. The later mechanism can be dominating depending on the topography of the cathode surface, which was confirmed by the erosion of the cathodes with 1200 µm grain size.

8:40am **SE+PS-ThM3 Self-organization of Plasma in RF Magnetron Sputtering*, Matjaz Panjan,*** Jozef Stefan Institute, Slovenia

Self-organization of magnetron plasma in so-called spokes has been previously reported for pulsed [1, 2] and continuous magnetron discharges [3]. In this presentation, we will demonstrate that spokes also form in oscillatory RF magnetron sputtering regime [4]. We used an ICCD camera and electrical probes to investigate the rotating plasma patterns. The spokes in RFMS were compared to the spokes in classical DCMS at similar discharge conditions. In both regimes, stable plasma patterns were observed for a wide range of discharge parameters. For similar gas pressures and discharge powers, the number of spokes in the RFMS regime was always larger than in the DCMS regime. The number of spokes changed sequentially with the increasing working gas pressure for both magnetron operations. In the DCMS regime, a single spoke was observed at the lowest argon pressure (0.25 Pa) and a second spoke was observed only at the highest pressure (2 Pa). In the same pressure range, the plasma in the RFMS regime displayed four spokes at the lowest pressure and six or seven spokes at the highest pressure. The influence of discharge power on the number of spokes was less pronounced for both magnetron regimes. Spoke patterns were analyzed by examining the inelastic collisions between electrons and argon atoms. For this purpose, we simulated the dissipation of electron energy in the drift direction and compared the calculations to the length and number of spokes for particular discharge conditions. Overall, the simulations agree well with the observed plasma patterns in DCMS and RFMS.

[1] A. Anders *et al.*, *J. Appl. Phys.*, **111** (2012) 053304

[2] A. Ehiasarian *et al., Appl. Phys. Lett.*, **100** (2012) 11410

[3] M. Panjan *et al.*, *Plasma Sources Sci. Technol.*, **24** (2015) 065010

[4] M. Panjan accepted for publication in *J. Appl. Phys.* (2019)

9:00am **SE+PS-ThM4 Study of High Power Pulsed Magnetron Sputtering Discharge with Positive Bias on the Target after the Main Pulse*, Ivan Shchelkanov,*** *T.J. Houlahan, J. McLain, I.F. Haehnlein, B.E. Jurczyk, R. Stubbers,* Starfire Industries LLC*; D.E. Barlaz, D.N. Ruzic,* University of Illinois at Urbana-Champaign

Low-pressure magnetron sputtering is a well-established industry standard for high quality thin film deposition. Among different types of magnetron sputtering, High Power Pulsed Magnetron Sputtering (HPPMS), also called High Power Impulse Magnetron Sputtering (HIPIMS), offers the highest ion fraction of sputtered material, which dramatically increases the options available for thin film synthesis. The highly ionized sputtered material assists in multilayer film growth leading to more adhesive, dense, and smoother films as compared to conventional DC Magnetron Sputtering (dcMS) techniques, without the need for extra plasma-assisting elements and techniques in the process. Unfortunately, HPPMS typically suffers from low deposition rates as compared to dcMS[1]. Various attempts have been made to overcome this drawback, among them are: more efficient magnetic field configurations [2-6], HPPMS operation with extreme target conditions [7,8], or the application of a pulsed positive bias onto the sputtered target to control the plasma potential after the main HPPMS pulse [9]. Operation with a positive voltage KICK at the end of the main HPPMS pulse allows for the deposition of multilayer coatings onto a cold, grounded substrate with better adhesion than is typical of a simple HPPMS discharge. Furthermore, for grounded substrates positioned at glancing angles with respect to the sputtered magnetron cathode, the deposited coatings exhibit a very dense structure and great adhesion to the substrate even when deposited onto the inside wall of high aspect ratio vias. To fully understand limits, effects, and drawbacks of the positive KICK, its influence on plasma parameters, deposition rate, coatings structure, and adhesion are discussed.

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[4] J. McLain, et al., Vacuum, Volume 155, Page 559-565 (2018)

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[8] A.V.Kaziev et al., Surface and Coatings Technology. 2016. Vol. 293. P. 48–54

[9] B. Wu et al., Vacuum, Volume 150, Page 216-221 (2018)

9:20am **SE+PS-ThM5 Innovative PVD Strategies for the Design of Novel TiO_2-based Photoanode Utilized in Dye-sensitized Solar Cells**, ***Rony Snyders***, University of Mons, Belgium **INVITED**

In view of the environmental challenges that our societies face, it is accepted that the development of alternative and renewable energy sources is a must. If solar energy is recognized as one of the most promising, it is still necessary to improve the solar cell technologies. Among others, Dye Sensitized Solar Cells (DSSC) are often seen as one of the ideal technological approach if several issues are fixed. One of the key problem associated with the implementation of these cells if related to the photoanode performances, specifically in terms of charge transport. Indeed, the standard photoanode based on TiO powder often exhibit a too high electrical resistivity associated with the intrinsic properties of the material.

During the past years, we have worked on the development of alternatives TiO_2-basedmaterial in order to solve the encountered problems. More precisely we have studied the growth of (N-doped) nano-sculpted TiO_2 films by using reactive magnetron sputtering in glancing angle deposition. Concerning the doping, co-reactive deposition as well as ion implantation have been evaluated. All samples have been thoroughly characterized by state-of-the-art techniques and, for most of them, tested in DSSCs.

The results demonstrate that our approach is versatile allowing to control the morphology of the TiO_2 films at the nanoscale, and therefore to tune the capability of the material to adsorb the active dye. Specifically, we showed that a combination of our films with conventional TiO_2 nanoparticles could be a promising approach. In addition, we also demonstrate that the phase constitution of the nano-sculpted films can be optimized in the form of a core-shell anatase/rutile structure in order to improve the charge transport. On the other hand, the study of the N doping reveals that it is possible to finely control the position of the N atom (substitutional vs intersticial) as a function of the experimental parameters. In this context, we demonstrated that the O vacancies density favor the substitutional doping. Finally, w e even showed that p type TiO_2:N films presenting good electrical and optical properties can be synthesized. This last result is of particular interest for the development of “full TiO_2” tandem DSSCs.

11:00am **SE+PS-ThM10 Enhancing the Far 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, S.G. Rosenberg,* American Society for Engineering Education (residing at U.S. Naval Research Laboratory); *J. del Hoyo, J.G. Richardson, M.A. Quijada,* NASA Goddard Spaceflight Center; *S.G. Walton,* U.S. Naval Research Laboratory

Astronomical measurements in the Far Ultra-Violet (FUV, 90-200nm) require the use of 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 desirable 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 metal reflector. XPS measurements indicate that this approach is capable of producing very thin (<5 nm) AlF_3 films with some mild (<10%) oxygen contamination. We will discuss the impact of plasma power, plasma chemistry, and plasma exposure time on the composition and structure of the passivation layer and how those parameters effect the optical properties. This work is partially supported by the Office of Naval Research, the Naval Research Laboratory base program, and NASA Strategic Astrophysics Technology (SAT) grant No. NNH177ZDA001N

11:20am **SE+PS-ThM11 Improving the Crystallinity of Inorganic Coatings Synthesized by Atmospheric Plasma using a New Device for Heating the Substrate**, ***Antoine Remy***, *M.S. Fall, F. Reniers,* Université Libre de Bruxelles, Belgium

The deposition of good quality crystalline inorganic coatings by atmospheric pressure dielectric barrier discharge remains a challenge. Thanks to an original coupling of a substrate heating device based on an inductive current loop and located under the dielectric and an atmospheric pressure dielectric barrier discharge, we show that one can deposit in one step crystalline vanadium oxide and titanium oxide, with grain sizes bigger than those achieved by post-deposition annealing. As case study, vanadium oxide and titanium oxide are chosen. The respective precursors (vanadium oxytriisopropoxide - VOTP and titanium tetraisopropoxide – TTIP) are injected as vapors in a home made reactor with argon acting as carrier gas and main plasma gas. Oxygen is injected as reactant in the chamber. The DBD operates using a G10S-V AFS generator, at a frequency of 19 kHz, and with an injected power comprised between 0 and 80 W. The heating unit consists in a inductively coupled device located under the bottom electrode and dielectric and a susceptor place between the substrate and the dielectric. Thanks to a modified design of the bottom electrode, the induction loop does not heat said electrode, but the Eddy current heats only the susceptor, and the substrate. It is shown that this device allows the direct synthesis of crystalline orthorhombic V_2O_5 at 300°C, and of anatase TiO_2 at 400°C. A comparison with coatings deposited at room temperature and annealed at 300 and 400°C respectively shows that the coatings deposited on the heated substrate exhibit larger grain sizes. This original combination of an atmospheric pressure plasma DBD and a device to heat inductively the substrate shows that one can obtain good crystallinity for inorganic coatings, and opens potentially new opportunities for the deposition of such coatings by atmospheric plasma.

11:40am **SE+PS-ThM12 Improved Nitride Formation on Titanium Substrates by Femtosecond Laser Processing with Secondary Plasma**, ***Jeremy Mettler***, *D.E. Barlaz,* University of Illinois at Urbana-Champaign; *B.E. Jurczyk,* Starfire Industries LLC; *D.N. Ruzic,* University of Illinois at Urbana-Champaign

We discuss the development of a plasma-enhanced, laser-induced surface conversion process for forming TiN, a common coating favored for its hardness and corrosion resistance. This process uses a pulsed femtosecond laser to provide localized energy deposition at the Ti surface, along with a secondary plasma to supply reactive N species. This method allows the surface conversion to be conducted in a single pass, rather than requiring a pretreatment step in Ar atmosphere for oxygen removal. The nitrogen radicals react preferentially where the laser provides sufficient energy to cause conversion of the native oxide layer. The conversion efficiency was investigated for DC and RF plasmas, as well as for different plasma powers, pressures, N precursors, and sample biases. Preliminary results with no secondary plasma achieved surface conversions of up to 9% TiN, measured using XPS. The inclusion of a secondary plasma provides a marked improvement over this previous result, both in terms of oxide removal and nitride formation. Laser powers for this work were between 3-5 W. A Langmuir probe diagnostic was used to compare plasma density at different powers (on the order of 100 W) and for different compositions.

12:00pm **SE+PS-ThM13 Characterizing the Spatially Dependent Properties of Plasma Polymerized Acrylic Acid Films**, ***Karyn Jarvis***, *S.L. McArthur,* Swinburne University of Technology, Australia

Plasma polymer films have been deposited on planar surfaces for a wide variety of applications, such as controlling cell growth or adding linker molecules for biosensors. They can however also be deposited onto three dimensional objects, such as tissue engineering scaffolds, biomedical implants or 3D printed devices. Coating three dimensional objects however is more complex as greater monomer fragmentation occurs closer to the electrode. It is therefore important to understand the properties of the plasma polymer films that will be deposited when a sample is different distances from the electrode. The use of plasma polymer films in biomedical applications also requires suitably stable films under physiological conditions, which will also be influenced by the distance from the electrode. Significant changes in film properties in aqueous conditions have serious implications on the incorporation of these films in biomedical devices.

Acrylic acid is a commonly used monomer for plasma polymerization to produce negatively charged carboxylic acid terminated surfaces, which have been used for a number of biomedical applications by manipulating cell growth. To gain a greater understanding of the spatially dependent behavior of plasma polymerized acrylic acid (ppAAc) films deposited in our custom-built stainless steel T-shaped reactor, ppAAc films were deposited at varying distances from the electrode (30 – 190 mm) at different deposition powers (5 – 80 W). The surface chemistry was analysed with X-ray photoelectron spectroscopy (XPS) while the film thickness was determined using spectroscopic ellipsometry. Aqueous stability was determined via immersion in Milli-Q. The film thicknesses decreased while the carboxyl group concentrations increased as the distance from the electrode increased and/or the deposition power decreased due to reduced monomer fragmentation further from the electrode and at lower powers. The aqueous stability of the films deposited further from the electrode increased as the deposition power increased. At 10 W, the film 30 mm from the electrode showed no decrease in film thickness after aqueous immersion while the films deposited 110 and 190 mm from the electrode were completely removed. Minimal film loss for the films deposited at 110 mm required a deposition power of 30 W while 60 W was required for minimal film loss for films deposited at 190 mm from the electrode. This work highlights the importance of having a spatially well characterized plasma reactor to enable the deposition of plasma polymer films with the desired properties, which has significant implications on the incorporation of these films into a number of applications.

2D Materials
Room A216 - Session 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA
Surface Chemistry, Functionalization, Bio, Energy and Sensor Applications

Moderator: Mark Edmonds, Monash University, Australia

2:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA1 Molecular Layers on Nanoporous Gold Electrodes***, **Elizabeth Landis**,* College of the Holy Cross

Nanoporous gold presents a surface with high conductivity and surface area, which makes it an interesting platform for surface chemistry. However, the nanoporous gold surface lacks the functionality necessary for many applications including sensing. We have investigated self-assembled thiol-based monolayers and the electroreduction of diazonium-based salts to form aryl molecular layers on nanoporous gold. We use infrared spectroscopy and cyclic voltammetry to show that the molecular layer ordering and density depends on the functionalization method, and the underlying nanoporous surface impacts molecular ordering and electron transfer properties.

2:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA2 Thermotropic Liquid Crystal (5CB) on Two-dimensional Materials***, **Paul Brown**,* American Society for Engineering Education*; S. Fischer, J. Kołacz, C.M. Spillmann, D. Gunlycke,* U.S. Naval Research Laboratory

Current means of redirecting light often rely on either bulky mechanical gimbals or non-mechanical diffractive elements. The former often suffer from wear and are susceptible to failure, while the latter may have significant optical power confined within side lobes. One promising non-mechanical approach that can overcome present limitations in beam redirection incorporates liquid crystal (LC) for continuous, refractive steering. Nematogens, the molecules comprising the LC in a nematic phase, support inherent anisotropic optical and dielectric properties that result from local ordering of single molecules. Recent research suggests the possibility of including two-dimensional materials to act as both an alignment layer and electrode to LC. This offers the possibility of further reducing device dimensions and device response time. Yet little research has focused on the ground state properties of a nematogen interfacing with the two-dimensional substrate. In this talk, we present density functional theory results of the electronic properties of a well-known nematogen (5CB) interacting with graphene, boron nitride, and phosphorene. We also discuss the influence of an introduced single vacancy on the electronic properties of the composite system. We find that 5CB on phosphorene offers the strongest binding of the considered nanosheets. Moreover, we observe qualitatively different band alignments, and focus in particular on type I, which prohibits free carrier transfer between the substrate and nematic LC. Lastly, we discuss the impact of single vacancies on the performance of two-dimensional materials to operate as both an alignment layer and electrode for LC-based applications.

This work has been supported by the Office of Naval Research, directly and through the U.S. Naval Research Laboratory.

3:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA3 Is it Possible to Achieve Intra-molecular Resolution with Ambient AFM?***, **Vladimir Korolkov**,* Oxford Instruments-Asylum Research*; S.C. Chulkov, M. Watkins,* University of Lincoln, UK*; P.H. Beton,* The University of Nottingham, UK

Although achieving molecular resolution is now almost a routine across various SPM imaging modes, resolving the actual molecular structure at the atomic level has only been accomplished with NC-AFM in UHV often at low temperatures and with a functionalized probe. Of course, the ultimate goal in SPM is to resolve the chemical structure of a molecule identifying each atom.

In this work we are presenting an approach to achieve intra-molecular resolution on adsorbed molecules in the ambient at room temperatures with a standard AFM cantilever with unmodified tip. We have discovered that using a combination of higher eigenmodes and low oscillation amplitudes (~3-5Å) of a standard Si-cantilever routinely provides ultra-high resolution on adsorbed molecules on surfaces[1,2] and bulk polymers[3].

With this approach we have been able to observe both intra-molecular features and inter-molecular contrast in thin films of coronene and melem molecules on the surface of hexagonal boron nitride (hBN). In case of coronene, all six benzene rings have been resolved as well as underlying atomic lattice of hBN. Unlike coronene, melem forms molecular assemblies with square symmetry stabilized with in-plane strong hydrogen bonds between amino groups. We have observed a strong inter-molecular contrast where the hydrogen bonds are expected to be. Similar to coronene, the observed intra-molecular contrast was associated with three triazine rings. We have used Probe particle model[4] to simulate our experimental AFM images and found very good agreement between them. In fact, PPM allowed us a correct interpretation of melem square phase assembly.

Both systems were studied at room and elevated temperatures where we observed phase transitions leading to thermodynamically stable systems. The experimental results are in excellent agreement with density functional theory calculations.

We believe the proposed approach, yet still in its infancy, could potentially provide a pathway to unambiguous identification of molecules on surfaces in the ambient on standard AFM systems.

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[1]Korolkov et al., Nat. Chem., 2017

[2]Korolkov et al., Nat. Comm., 2017

[3]Korolkov et al., Nat. Comm., 2019

[4]Hapala et al., Phys. Rev. B 90, 085421

3:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA4 Tailoring Surface Properties via Functionalized Hydrofluorinated Graphene Compounds***, **Jangyup Son**,* University of Illinois at Urbana-Champaign*; N. Buzov,* University of California at Santa Barbara*; S. Chen,* University of Illinois at Urbana-Champaign*; D. Sung,* Sejong University, Republic of Korea*; H. Ryu,* Seoul National University, Republic of Korea*; J. Kwon,* Yonsei University, Republic of Korea*; S. Kim, J. Xu,* University of Illinois at Urbana-Champaign*; S. Hong,* Sejong University, Republic of Korea*; W. King,* University of Illinois at Urbana-Champaign*; G.H. Lee,* Seoul National University, Republic of Korea*; A.M. van der Zande,* University of Illinois at Urbana-Champaign

Mixing compounds or alloys is an important process to tailor or enhance the intrinsic properties of materials such as chemical reactivity, mechanical strength, and electronic structure. In nanosystems, such as two-dimensional (2D) materials like graphene, transition metal dichalcogenides (TMDCs), and hexagonal boron nitride (hBN), where there is no distinction between the surface and the bulk, mixing of elements is also an important tool for tailoring the interaction of the material with its environment. A successful strategy for manipulating the chemical structures of 2D materials is the chemical functionalization of graphene with single elements such as H, O, N, and F. Yet, an even wider parameter space is possible by combining these functionalization species to produce ternary functionalized graphene compounds.

Here we present a new strategy for producing functionalized graphene compounds through the systematic control of the ratio between adatoms. We demonstrate tailored hydrofluorinated graphene (HFG) compounds via the sequential exposure of graphene to low-energy hydrogen plasma and xenon difluoride (XeF_2) gas. We demonstrate reversible switching of the surface between completely hydrogenated graphene (HG) and fluorinated graphene (FG) as well as the intermediate ratio between two extremes. Moreover, we demonstrate pattern the surface functionalization on a single chip into chemically distinct materials (graphene, FG, HG, and HFG compounds).

Finally, with these patterned structures, we demonstrated tailoring of the surface and electronic properties of the 2D materials. First, the patterned structures enable direct comparisons of the relative surface properties such as wettability and surface friction. Additionally, the electrical properties of functionalized graphene compounds showed unusual recovery of electrical conductance during the partial transformation of FG to HFG, due to initial removal of existing F adatoms when exposed to hydrogen plasma. This study opens a new class of 2D compound materials and innovative chemical patterning that can lead to atomically thin 2D circuits consisting of chemically/electrically modulated regions.

4:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA7 Towards Higher Alcohol Synthesis from Syngas on 2D material-based catalysts: A First-Principles Study****, **Tao Jiang**, D. Le, T.S. Rahman,* University of Central Florida

Synthesis of higher alcohol from syngas has been of great interest owing to the limited petroleum resources and environmental concerns. Rational designing of cheap and efficient catalyst material for such synthesis is in great demand because of diminishing supply of the current state-of-the-art catalysts. Two dimensional (2D) materials are emerging with far-reaching potential for technical and industrial applications thanks to their unique properties, recent developments and improvement of production technologies. In this talk, we will discuss our recent work, based on first

principles calculations, towards the unitization of 2D materials as catalysts for higher alcohol synthesis. In particular, defect laden hexagonal boron nitride (*dh*-BN) with N vacancies is excellent catalyst for hydrogenation of CO_2 towards ethanol formation, in the reaction pathway of which thecrucial step for forming C_2 bond, i.e. reaction of adsorbed species CH_3* and CO* to form CH_3CO*, is exothermic with reasonably low activation barrier (0.68 eV). On the other hand, we also find single layer of MoS_2 functionalized with small Au nanoparticle to catalyze CO hydrogenation reaction towards ethanol formation. Among all the elementary reactions, the important steps are the reaction of an adsorbed CH_3* and a CO* molecule and the hydrogenation of acetyl to acetaldehyde (both are exothermic with activation barriers of 0.69 and 0.47 eV, respectively) to form C_2 species.[1] The results suggest that 2D materials are suitable candidates for higher alcohol synthesis. Full reaction pathways will be discussed together with results of Kinetic Monte Carlo simulations to shed light on the selectivity of the catalysts. Contact will be made with experimental data that validate our theoretical predictions.

[1] K. Almeida, K. Chagoya,A. Felix, T. Jiang et al, "Towards Higher Alcohol Formation using a single-layer MoS_2 activated Au on Silica: Methanol Carbonylation to Acetaldehyde", submitted

*Work supported in part by DOE Grant DE-FG02-07ER15842

4:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA8 Proton Conductivity Properties of Electrospun Chitosan Nanofibers**, ***Woo-Kyung Lee**, J.J. Pietron, D.A. Kidwell, J.T. Robinson, C.L. McGann, S.P. Mulvaney,* U.S. Naval Research Laboratory

A major challenge of the 21st century will be to establish meaningful two-way communication between biology and electronics. The study of protonics, devices that mimic electronics but pass protons instead of electrons, seeks to bridge this gap. Protonic conductive materials (PCMs) are essential elements of these devices and we have demonstrated significant improvement in conductivity for chitosan PCMs when deposited as electrospun nanofibers. The observed improvements stem from both enhanced molecular alignment and from chemical doping due to the electrospinning carrier fluid, trifluoroacetic acid (TFA). We deposited electrospun chitosan nanofibers over palladium protodes and then used the helium ion microscope to isolate single nanofibers for detailed study. We observed that single chitosan nanofibers are strongly doped by TFA with x-ray photoelectron spectroscopy demonstrating extensively protonated nitrogen functionality. With the isolated, single chitosan nanofibers we observed that water uptake, fiber/electrode contact area, and doping concentration are critical parameters of protonic device performance and lead to increased conductivity (*i.e.* low resistivity). The average resistivity of single chitosan nanofibers is 6.2×10^4 Ω·cm, approximately two orders of magnitude lower than the resistivity of cast chitosan PCMs (cast from acetic acid solutions not TFA).We have observed excellent agreement between theoretical models and experiment results that explore each of the contributions to the improved conductivity. In addition, the fabrication and measurement of ionic field-effect transistor of single chitosan fiber using conductive atomic force microscope will be discussed.

5:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA9 Sensor for Breath and Skin Diagnostics**, ***Pelagia I Gouma,*** The Ohio State University

Resistive gas sensors have received a bad reputation of being largely non-selective.

Our work has produced a crystallo-chemical model for selective gas sensing by polymorphic

metal oxides. The reaction-based and ferro-electric poling sensing mechanisms are discussed

in detail. Novel processing methods to produce the respective nano sensors are presented along

with the device fabrication for the non-invasive diagnosis of gaseous biomarkers in human

and animal breath or skin. This sensor technology is expected to revolutionize medical diagnostics.

5:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA10 Symmetry Controlled Ddsorption of Diodobenzene on MoS_2**, ***Zahra Hooshmand,*** University of Central Florida*; P. Evans, P.A. Dowben,* University of Nebraska - Lincoln*; T.S. Rahman,* University of Central Florida

In a joint experimental and theoretical study, we have uncovered evidence of the importance of symmetry in the adsorption of the isomers of diiodobenzene on MoS_2(0001). The intensity ratio of iodine to molybdenum measured, as a function of exposure for different isomers of the diiodobenzene, show that while for ortho (1,2-) and para (1,4-) diiodobenzene the rate of adsorption at 100 K is very low, that for meta (1,3-) diiodobenzene is considerably more facile. We have applied dispersion corrected density functional theory-based calculations to understand the subtleties in the electronic structure and geometry of adsorption of these diiodobenzene isomers on MoS_2(0001). All three isomers are found to weakly chemisorb with the same binding strength as well as adopt similar configurations. The calculated electron affinity of the three molecules also do not show a specific trend that would verify experimental data. However, analysis of the frontier orbitals indicate that those of 1,3-diiodobenzene are strongly affected by interactions with MoS_2, while that of the other two isomers remain unchanged. Our results show that symmetry is the identifying factor in these adsorption characteristics. The results of frontier orbitals analysis confirm that for adsorption of (1,2-) and (1,4-) diiodobenzene a reduction in the symmetry of the adsorbent is needed. To further validate our conclusions, we compare the above results with that of the adsorption of the diiodobenzene isomers on defect-laden MoS_2(0001).

* Work support in part by DOE grant DE-FG02-07ER15842

5:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA11 Mechanistic Understanding of the CO Hydrogenation Reaction on Defect Engineered 2D-TaS_2 and 2D-MoS_2 Catalysts**, ***Mihai Vaida,*** University of Central Florida

Due to global energy demands, investigation of catalytic reaction mechanisms on novel catalytic materials that can lead to efficient production of storable fuels from sustainable inputs is of central importance. In this contribution the adsorption of CO and H_2 molecules, as well as the CO hydrogenation reaction are investigated on defect engineered two dimensional (2D) TaS_2 and MoS_2. Crystalline 2D-TaS_2 and 2D-MoS_2 with surface area of 1 cm^2 are synthesized via a multistep process based physical vapor deposition on Cu(111). The surface composition, morphology, and electronic structure are investigated via Auger electron spectroscopy, low energy electron diffraction, scanning tunneling microscopy, scanning tunneling spectroscopy, and photoemission spectroscopy. The interaction of the molecules with the surface and the catalytic reaction mechanisms are investigated via temperature programmed desorption/reaction. No catalytic reactions have been observed on crystalline 2D materials. However, an enhanced catalytic activity is observed after the generation of sulfur vacancies via Ar sputtering. The CO hydrogenation on TaS_2 occurs on low coordinated Ta atoms through the formation of formyl radical (HCO) and formaldehyde (HCOH). On 2D-MoS_2, the CO hydrogenation also occurs on low coordinated Mo atoms. However, in this case the formyl radical splits to form methyldyne radical (CH), which subsequently react with other CH radical to produce acetylene (C_2H_2).

Plasma Science and Technology Division
Room B130 - Session PS+2D+EM+SS+TF-ThA

Plasma-Enhanced Atomic Layer Etching

Moderators: Steven Vitale, MIT Lincoln Laboratory, Mingmei Wang, TEL Technology Center, America, LLC

2:20pm **PS+2D+EM+SS+TF-ThA1 Atomic Layer Etch: Real World Utilization of an Idealized Solution**, ***Peter Biolsi,*** TEL Technology Center, America, LLC **INVITED**

Atomic Layer Etch: Real World Utilization of an Idealized Solution

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. Atomic layer etching (ALE) has gained favor as an approach to extract more control over the fabrication of small CD complex topographic structures, atomic later etching. 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. For the etching of dielectric materials, a self-limiting precursor step is not available as etch processes relies on cyclic process (fluorocarbon deposition and ion bombardment steps). 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 with additional burden of throughput.

Even though ALE can be difficult to be utilized in real-word scenarios, the learning from ALE finds its use in many etch applications. An etch chamber which can provide wide range of radical to ion flux ratios and precise ion energy control (using pulsing techniques) is suitable for ALE or utilizing ALE learnings. Currently, new ALE techniques based on surface modification by ions (Hydrogen plasma treatment of Silicon Nitride) followed by removal of modified layer by F radicals (High pressure NF3 or SF6 plasma) or surface modification by NH3/HF (to create a quasi-self-limiting diffusion barrier layer) followed by removal of modified layer by thermal means, are employed to etch critical layers where requirements are stringent. New frontier of etch technology will be the ability to achieve area selective etch without compromising etch rate of the process. Examples of such activities will be presented in this presentation.

3:00pm **PS+2D+EM+SS+TF-ThA3 Mechanism of SiN Etching Rate Fluctuation in Atomic Layer Etching**, ***Akiko Hirata***, *M. Fukasawa, K. Kugimiya, K. Nagaoka,* Sony Semiconductor Solutions Corporation, Japan; *K. Karahashi, S. Hamaguchi,* Osaka University, Japan

Atomic layer etching (ALE) enables atomic-precision control of the surface reaction and low damage etching of the underlying layer for device fabrication. In this study, we investigated SiN ALE with process optimization of the surface adsorption and desorption steps, and we clarified the rate fluctuation mechanism.

A dual frequency CCP reactor (60 MHz/2 MHz) was used in this study. A SiN (50 nm) was deposited on the Si substrate by LPCVD. One etching cycle consisted of two steps. CH_3F/Ar plasma was applied to deposit the hydrofluorocarbon (HFC) polymer as the adsorption step. Then, Ar plasma was used in the desorption step. The thicknesses of SiN and the HFC polymer were measured by spectroscopic ellipsometry. The chemical bonding was analyzed by XPS.

A 1.2-nm-thick HFC polymer was deposited on SiN as the adsorption step. Next, we investigated the desorption step by using Ar plasma. The etched amount for 1 cycle was 0.58 nm. However, we found the etch-stop of SiN after 10 cycles of ALE, owing to the deposition (>6 nm) of a protective film on the surface. The etch-stop could be caused by sputtering of the Si upper electrode and/or re-deposition of the HFC film. To investigate the etch rate fluctuation, the SiN surface after ALE was analyzed. C-C and C-N bonds were detected after 1 cycle, and C-C bonds increased after 10 cycles. It was clear that the excess HFC polymer deposition suppressed the ALE reactions. Ar^+ ion bombardment during the desorption step selectively eliminated the H and F in the HFC polymer, because the bonding energies of C-H and C-F were low. As the bonding energies of C-C (6.4 eV) and C-N (7.8 eV) are relatively high, these bonds remained after the desorption step. We speculated that excess C-rich polymer deposition after ALE started from the residual C-C bond. Residual Si-C bond is also possible reason, since the MD simulation revealed that the formation of Si-C bond was promoted in the fluorocarbon layer during SiO_2 ALE. [1] These results clearly showed that the initial adsorption kinetics of HFC polymer was strongly affected by the residual carbon on the SiN surface. To suppress the C-rich polymer deposition, we studied stable SiN ALE using the desorption step of Ar/O plasma (0.36 nm/cycle) and the two-step sequential desorption step of Ar and O plasma (0.6 nm/cycle). Although the effect of O adsorption in SiO ALE has been studied previously,[2] few studies have been reported for the case of SiN. Because the surface condition is able to fluctuate with the number of cycles, precise surface control is strongly required to achieve stable ALE.

[1] S. Hamaguchi et al., 2018 AVS, PS-FrM6. [2]T. Tsutsumi et al., JVST A 35 (2017) 01A103.

3:20pm **PS+2D+EM+SS+TF-ThA4 Effect of Polymerization on Ar+ Bombardment Modification of SiO_2 and Si_3N_4 Substrates: Molecular Dynamics Simulation Study**, ***Hojin Kim***, *Y. Shi, Y.-H. Tsai, D. Zhang, Y. Han,* TEL Technology Center, America, LLC; *K. Taniguchi,* TEL Miyagi Limited, Japan; *S. Morikita,* TEL Miyagi Limited; *M. Wang, A. Mosden, A. Metz, P.E. Biolsi,* TEL Technology Center, America, LLC

To understand the selective removal of silicon oxide (SiO_2) against silicon nitride (Si_3N_4) with gaseous reactants for advanced etch process, we have studied the surface modification of both SiO_2 and Si_3N_4 substrates with Ar+ bombardment by using molecular dynamics (MD) simulation. The substrate samples was prepared with and without carbon (C) and hydrogen (H) polymerization to investigate the effect of polymerization on surface modification. C and H atoms were deposited with low ion energy not to disrupt the surface much. After preparation of substrate, Ar+ bombardment with various ion energy (IE) were performed. We obtained a damage depth with a wigner-seitz defect analysis as a function of IE and compared the cases with and without polymerization to check the role of the added polymer layer on surface modification. In pristine Si_3N_4 and SiO_2 case, at IE=25eV, both substrates starts to show the damage with penetration of Ar+ and follows with an exponential raise as the IE increases. Damage depth at Si_3N_4 is deeper than that at SiO_2. In polymerization, simulations show that H is more deposited than C on Si_3N_4 while on SiO_2, C is more deposited than H. no silicon-hydrogen bonds appear on both substrates and in Si_3N_4, nitrogen-hydrogen bond is dominated while oxygen-carbon bond is popular in SiO_2. For damage analysis, in Si_3N_4 case, CH polymerization helps to lower about 30% in the damage depth with exponential behavior. However, SiO_2 case shows the opposite effect of CH polymerization in the damage depth. Formed polymer layer leads to increase the damage depth by comparing with pristine SiO_2 and helps more clear exponential behavior as a function of IE. Finally, analyzed results using XPS and/or SIMS from blanket SiO_2 and Si_3N_4 films etched in a Capacitively Coupled Plasma (CCP) chamber are compared with the MD simulation results.

4:00pm **PS+2D+EM+SS+TF-ThA6 Advanced Cyclic Plasma Etch Approaches for Metal Patterning: Synergy and Surface Modification Effects**, ***Nathan Marchack***, IBM T.J. Watson Research Center; *K. Hernandez,* University of Texas at Dallas; *J. Innocent-Dolor, M.J.P. Hopstaken, S.U. Engelmann,* IBM T.J. Watson Research Center **INVITED**

Atomic layer etching or ALE is a burgeoning research area of plasma processing that offers critical advantages needed for future advancements in semiconductor devices, namely lower damage and enhanced selectivity, through its self-limited reaction cycles separated by purge steps.[1] ALE processes offer a significantly higher degree of tunability over traditional continuous-wave (CW) plasma etching, due to the fact that parameters such as gas flows, pressure, and bias power can be adjusted on a step-specific basis rather than as a global setting for the length of the process.

Our previous work investigated the effect of varying the purge step times in a quasi-ALE process using alternating Cl_2/H_2 exposures on the etched profiles of titanium and tantalum nitride.[2] Titanium and tantalum-based conductive films have been previously evaluated as gate materials for CMOS devices but more recently have been incorporated as top electrodes for novel technologies such as magnetoresistive RAM (MRAM) and hard masks for carbon electrodes utilized in biological sensing. As the trend of downscaling device size continues, the ability to pattern these films at tight pitches with minimal redeposition becomes highly important.

Sub-surface modification of films such as Si_3N_4 and indium-doped tin oxide (ITO) by low atomic weight (LAW) ions such as H^+ has been discussed in literature as facilitating self-limited etch behavior.[3,4] We present new data exploring the incorporation of LAW species into cyclic etch processes, namely penetration depth into these metal nitride films and their role in surface oxide formation, the latter of which can contribute to novel pitch multiplication schemes.[5] SIMS measurements reveal that the depth of penetration of H^+ for TaN films can be >40 nm and can occur through a native oxide layer that inhibits etching by Cl species. Pressure variation is a significant factor in tuning this effect, which can potentially modify the etch resistance of these films and enable novel integration schemes.

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4:40pm **PS+2D+EM+SS+TF-ThA8 Surface Modification and Stability of Plasma-assisted Atomic-layer Etching (ALE) of Si based Materials; Analysis by Molecular Dynamics (MD) Simulation**, ***Satoshi Hamaguchi***, *M. Isobe, E.J.C. Tinacba, S. Shigeno, Y. Okada, T. Ito, K. Karahashi,* Osaka University, Japan

A plasma-assisted atomic-layer etching (ALE) process typically consists of alternating application of chemically reactive species (adsorption step) and Ar ion bombardment with low bias energy (desorption step) to the surface to be etched. In the adsorption step, a modified layer is formed on the material surface and, in the desorption step, the modified layer is removed with the original material underneath being intact. In this presentation,

using the results of MD simulation of ALE for Si, SiO2, and SiN, together with experimental observations, physical mechanisms of the formation and removal of surface modified layers in typical ALE processes will be discussed.

Our molecular dynamics (MD) simulation of SiO2 ALE by fluorocarbon adsorption and Ar+ ion bombardment shows that preferential sputtering of oxygen takes place by Ar+ ion bombardment and a Si rich layer mixed with fluorine and carbon atoms is formed on the SiO2 surface. Ideally this modified layer should be removed completely in the subsequent desorption step, but in general it is not. In such a layer, the atomic number ratio of Si to O can be as high as unity and carbon provided in the subsequent adsorption step tends be deposited rather than removing O atoms from the surface by forming CO molecules. Therefore as the ALE cycles proceed, the adsorbed fluorocarbon layer thickens and eventually an etch stop may occur. With fine tuning of incident Ar+ ion energy, an etch stop may be avoided but the process window to achieve both continuous ALE cycles (by sufficiently high Ar+ ion energy) and ideal self-limit in each cycle (by sufficiently low Ar+ ion energy) may still be small or even nonexistent. The incompleteness of the modified surface removal in each ALE cycle seems universal phenomena for plasma-assisted ALE for most materials. For other plasma-assisted ALE processes that we examined by MD simulation, the surface modified layer formed during the adsorption step could not be removed completely by low-energy Ar+ ion bombardment, either. Indeed low-energy Ar+ ion bombardment contributes to the formation of a deeper modified layer by pushing down adsorbed species into the bulk, rather than simply removing it.

5:00pm **PS+2D+EM+SS+TF-ThA9 Innovative Future Etch Technology by Atomic-order Control***, **Yoshihide Kihara**, T. Katsunuma, S. Kumakura, T. Hisamatsu, M. Honda,* Tokyo Electron Miyagi Ltd., Japan **INVITED**

In recent years, with the progress of device miniaturization and increased challenges in the scale of integration of semiconductor devices, ultra-high selectivity and atomic layer-level critical dimension (CD) control techniques are required in the fabrication processes.

In the conventional etching, using a fluorocarbon (FC) gas, the high selectivity is obtained by taking advantage of the difference of the FC protective film thickness due to the difference of materials.[1] However, adopting the conventional approach to cutting-edge pattern structure becomes difficult due to the excessive FC film clogging the micro slit facet. To meet the highly complex requirements, alternative process was developed by using ion modification and chemical dry removal.[2] We have made several improvements on this new approach and applied it to SiN and SiC etching. The improved new approach achieves ultra-high selectivity without FC protective film and we also confirmed this process has the characteristics of a self-limiting reaction based on ion depth profile as well as ALE.

In the patterning processes, lower pattern densities have a larger CD shrinking due to micro-loading. Hence, we developed the new process flow that combines atomic layer deposition (ALD) technique and etching. With this method, we achieved CD shrinking at atomic-layer level precision for various patterns, without causing CD loading.[3]

Moreover, Quasi-ALE can etch the pattern while maintaining the mask CD for different pattern density. This is because Quasi-ALE precisely controls the surface reaction by controlling the radical flux and ion flux independently.[3] Also, it was necessary to control oval CD size between X and Y respectively. We found that X-Y CD control can be easily performed by changing the balance of FC adsorption and Ar desorption in Quasi-ALE. However, there are concerns about mask selectivity and ion damage in this approach. To solve these problems, we introduce the Advanced Quasi-ALE technique which combines mask protection together with Quasi-ALE. The Advanced Quasi-ALE achieves wider X-Y CD control margin.

On the other hand, as aspect ratio is increased in the memory fabrication process, the occurrence of bowing profile is a serious problem. To address the issue, the new improvement technique has been developed that combines the concept of ALD and etching. With this method, we are able to etch profile more vertically in high A/R feature.

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Plasma Science and Technology Division
Room B131 - Session PS+SS-ThA

Plasma Conversion and Enhanced Catalysis for Chemical Synthesis

Moderator: R. Mohan Sankaran, Case Western Reserve University

2:20pm **PS+SS-ThA1 Rate Limiting Factors of Low Pressure Plasma-catalytic CO_2 Methanation Process***, **Kazunori Koga**, A. Yamamoto, K. Kamataki, N. Itagaki, M. Shiratani,* Kyushu University, Japan

The methanation of CO_2 attracts attention as the ways of CO_2 reduction and energy storage as well as space exploration. It is expected to produce rocket propellant fuels at Mars and CO_2 conversion in space stations. The Sabatier reaction has been employed to generate CH_4 from CO_2 and H_2. Using catalysts realizes a high conversion efficiency. However, the conventional catalytic reaction starts at about 200 ^oC but thermal runaway occurs above 250 ^oC. The heat management is an important problem. A method using non-thermal plasma with catalyst allows methanation under low-temperature condition [1, 2]. Here, we studied rate-limiting steps of CO_2 methanation and their important parameters in the plasma-catalytic process. Experiments were carried out using a capacitively coupled plasma reactor. The electrode diameter was 50 mm and the distance between the electrodes was 6.1 mm. The Cu electrodes were employed as catalyst. We set a CO_2 gas flow rate between 1.0 sccm and 5.0 sccm and an H_2 gas flow rate between 1.0 sccm and 30 sccm. The pressure was 750 Pa. The discharge power was set in a range of 10 to 100 W. Gas composition in the discharge plasmas was measured with a quadrupole mass spectrometer. CH_4 yield rapidly increases with time after plasma initiation. It tends to be saturated after 200 s. From time dependence of catalyst temperature, the saturation occurs between 350 K and 370 K. The temperature shows the threshold temperature at which the rate-limiting step change from gas-phase reactions in plasma to surface reactions on the catalyst. The CH_4 yield increases with increasing the gas residence time. From optical emission spectroscopy, emission intensity related with CO angstrom band increase with the gas residence time but hydrogen-related emission is irrelevant to the residence time. It suggests that CO excited by plasma is responsible to the CH_4 yield increase. The results of H_2 gas flow rate dependence suggest that electron temperature is an important factor in the rate-limiting step of the gas phase reaction. I will discuss the detail mechanisms at the conference.

Work supported partly by JAXA and JST.

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2:40pm **PS+SS-ThA2 Radical Nitriding of Graphene Promoted by Surface Plasmon Resonance of Gold Nanoparticle Catalyst***, **Takeshi Kitajima**, T. Nakano,* National Defense Academy, Japan

In recent years, catalyst activity[1] of graphene nitride including fuel cell catalysts has attracted attention. We apply the catalytic property[2] of gold nanoparticles to the surface reaction of graphene, and investigate a process that can nitride graphene while reducing the damage caused by plasma irradiation.

In this study, we compared the degree of nitridation according to the presence or absence of ion irradiation (I), light irradiation from plasma (L) and the presence or absence of gold nanoparticle catalyst (C), respectively, and discovered the presence of radical nitriding by surface plasmon resonance of gold nanoparticles.

Gold is deposited for 2 minutes by electron beam evaporation on graphite crystals in an ultra-high vacuum chamber.

It was found by AFM measurement that gold nanoparticles with a diameter of about 20 nm were formed on the graphite crystal surface by aggregation.

Next, NH_3-Ar (1: 3) mixed plasma (ICP, 70 MHz, 100 W) at a pressure of 10 Pa was generated in the plasma chamber. The sample was irradiated for 10 minutes with radicals and light that passed directly or through a 30 line/inch SUS304 single mesh.

The atomic composition by XPS was examined for each irradiation condition. It was found that in the condition RLC where gold nanoparticles were generated and irradiated with radicals and light, nitridation was promoted about twice as much as plasma irradiation.

It is speculated that irradiation of gold nanoparticles with light excites plasmons to promote the nitridation reaction.

Next, Raman scattering analysis of graphene nitride was performed. Islands found on graphite were considered as graphene. Among the Raman scattering spectra, the component intensities of 2D (2690 cm -1), G (1580 cm -1) and D (1350 cm -1) were measured to evaluate the intensity ratio.

Under RLC conditions, the I2D / IG ratio has not dropped significantly. It can be seen that the structural change of the graphene island due to ion bombardment is prevented. Furthermore, the ID / IG ratio is higher than in plasma irradiation (RIL), and it can be confirmed that nitrogen doping has progressed more. From the above, it is considered that the catalytic activity of the gold nanoparticles is expressed by the effect of surface plasmon excitation, and the formation of graphene nitride with low damage by radicals becomes possible.

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2. Marie-Christine Daniel and Didier Astruc, Chemical Reviews 104, 293 (2004).

3:00pm **PS+SS-ThA3 Plasma-assisted Catalysis: Exploring the Effects of Plasma Stimulation on Catalyst Performance***, **Jason C. Hicks**,* University of Notre Dame **INVITED**

Plasmas create incredibly reactive chemical environments and have a long history in chemical synthesis and removal of volatile organic compounds.[1-2] Plasmas can be generated in the presence of a catalyst (plasma-assisted catalysis) to increase conversions and improve the selectivity to desired products. Our research in the area of plasma-assisted catalysis is focused on the ability to control the catalyst performance by tuning the plasma environment or plasma-catalyst interactions.[3-4] We have been particularly interested in the use of non-thermal plasmas for C-H and N_2 activation via dry reforming of methane and ammonia synthesis reactions, respectively. Specifically, this presentation will focus on 1) the reaction regime where catalyst-plasma interactions are observed for these reactions, 2) the various catalyst-plasma interactions observed, and 3) the role of the plasma in enhancing reaction efficiency. This presentation will highlight our recent progress in controlling plasma-catalyst interactions to enhance reaction efficiency.

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(2) Mehta, P.; Barboun, P.; Go, D. B.; Hicks, J. C.; Schneider, W. F. ACS Energy Lett. **2019** 5, (4)

(3) Mehta, P.; Barboun, P.; Herrera, F. A.; Kim, J.; Rumbach, P.; Go, D. B.; Hicks, J. C.; Schneider, W. F. *Nat. Catal.***2018**, No. 4.

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4:00pm **PS+SS-ThA6 A Plasma-aerosol Droplet Reactor for the Synthesis of Ammonia from Nitrogen and Water***, **Joseph Toth**, D.J. Lacks, J. Renner, R.M. Sankaran,* Case Western Reserve University

Alternative approaches are sought to the high-pressure, high-temperature Haber-Bosch (H-B) process for nitrogen fixation in order to enable distributed synthesis from renewable feedstocks. A potentially promising reactive strategy is plasma excitation which was historically the first method to fix nitrogen by reacting nitrogen and oxygen in air. More recently, plasmas have been combined with solid catalyst materials to synthesize ammonia at atmospheric pressure and lower temperatures than the H-B process. However, most of these reactions still require hydrogen gas which remains linked to fossil fuels and leads to both high cost and environmental consequences.

Here, we present a novel plasma-aerosol droplet reactor to synthesize ammonia from nitrogen and water at atmospheric pressure and near room temperature. Introducing the water as droplets instead of water vapor increases the throughput that can be achieved and also simplifies the system, eliminating the need for heated lines to avoid condensation on the walls. The plasma was formed as a dielectric barrier discharge inside a quartz tube with an outer ring electrode and an inner wire electrode. The water droplets were generated using a commercial nebulizer via a high nitrogen flow rate causing a Venturi effect which siphoned the water into the gas stream. The products were collected by bubbling the gas effluent leaving the reactor through a concentrated sulfuric acid bath and condensing in a second trap chilled to -40 ºC. The ammonia was then measured by the *o*-phthalaldehyde colometric assay technique. The ammonia production rate was found to be a function of the power and flow rate with production rates up to 600 µg/hr at 70 W. Controls were run with an argon plasma and with no water droplets to verify that no ammonia was produced without both nitrogen and water. In addition to ammonia, we also tested for nitrites/nitrates (NO_x) and measured up to 3000 µg/hr total production rate. The efficiency, power consumption, and potential reaction mechanisms will also be discussed.

4:20pm **PS+SS-ThA7 Plasma-assisted Nitrogen Fixation by Water: Development and Evaluation of Hybrid Membrane Based Plasma-Electrochemical Reactor***, R. Sharma, **Richard M.C.M. van de Sanden**, H. Patel, V. Kyriakou, U. Mushtaq,* Dutch Institute for Fundamental Energy, Netherlands*; A. Pandiyan,* Dutch Institute for Fundamental Energy*; S. Welzel, M.N. Tsampas,* Dutch Institute for Fundamental Energy, Netherlands

The worldwide energy crisis and environmental issues have greatly driven the current research on exploring and efficiently utilizing the environmentally-friendly and sustainable energy sources[1]. Most sustainable sources such as solar and wind energy are in principle able to meet the global energy demand. Nevertheless, they are intermittent and require new concepts of conversion and storage of electricity. Storing energy in form of chemical bonds is considered as an effective option for long term storage. Thus there is quest of developing effective processes for converting electrical energy into molecules.

In this context, nitrogen fixation is unquestionably one of the most important chemical conversion process since it converts N_2 into molecules of high energy (e.g. NH_3, NO)[2]. However, contemporary chemical industry for nitrogen fixation imposes great concerns about the environmental sustainability in terms of immense energy consumption and burdened emissions profile. Nevertheless, plasma-technology has been receiving renewed attention as an alternative “green” approach for N_2 activation which is one of the fundamental requirement for nitrogen fixation.

Up to now solutions were mainly sought on material axis, however recent theoretical studies have revealed that there are intrinsic limitations of catalysis (i.e. scaling relationships) which keep the processes far from the optimum performance. In this work, we will present a unique solution to the aforementioned limitations by employing a hybrid type reactor consisting of a plasma reactor and solid state water electrolysers with oxygen ion[3] or proton conducting membranes. Unlike conventional plasma catalysis that requires the co-activation of reactants, in the proposed alternative approach, electrolysers provide reacting species on catalysts with a controllable manner while a radiofrequency plasma is used to increase the reactivity of N_2. Such spatial separation of N_2 dissociation and catalytic formation of the target molecules provides truely independent parameters to optimise the nitrogen fixation process. One aided benefit of the proposed approach is that both technologies, i.e. water electrolyser and plasma activation, utilize base molecules (N_2 and H_2O) and can be directly powered by renewable electricity. Such a scheme may be a stepping stone to zero carbon footprint processes. Moreover, the advantages of proposed approach will be also compared to conventional plasma catalysis or pure plasma processes.

References

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4:40pm **PS+SS-ThA8 Plasma-Assisted Ammonia Synthesis in Hybrid Plasma-Catalysis DBD Reactors***, Z. Chen, X. Yang, Y. Ju, S. Sundaresan, **Bruce E. Koel**,* Princeton University **INVITED**

Solar and wind power are creating increasingly large amounts of electricity, and an important question is how can we take advantage of the expanding increase of renewable electricity for catalysis? One approach is plasma-assisted catalysis, which utilizes excited gaseous molecules or new reactive species formed in a (non-equilibrium, low temperature) gas discharge plasma, along with a catalyst to enable increases in the activity and selectivity for carrying out desirable chemical reactions. A significant challenge in plasma-catalysis hybrid systems is to achieve the strongest synergistic interactions between the plasma and catalyst to increase performance and overall energy efficiency. We report on two types of dielectric barrier discharge (DBD) reactors (with a coaxial tube and parallel plates) that have been used to screen catalytic effects of different metal surfaces and supported catalysts in plasma-catalysis hybrid systems at near atmospheric pressure, utilizing both AC and nanosecond pulsed discharges. We observed strong synergistic effects between non-equilibrium plasma and catalysts for both NH_3 synthesis and methane coupling reactions. We compared the performance for ammonia synthesis of catalysts using active metals (Pd, Pt, and Fe) or less active metals (Au, Ag, and Cu) or their alloys.

We found that the metal-nitrogen (M-N) bond energy was not the only parameter governing the catalytic activity for NH_3 synthesis in plasma. Better catalytic activity could be achieved by bimetallic catalysts that contained catalytic sites for both N_2* dissociation and hydrogenation of M-N bonds, leading to our observations of a highly active PdFe catalyst for NH_3 synthesis in plasma. In addition, we will also report briefly about results in CO_2 reforming of methane in the coaxial reactor, where we found that under thermal only conditions, $PtFe/Al_2O_3$ catalyzed mainly the formation of CO and H_2, but with the plasma on, the selectivity shifted to methane coupling reactions. Interestingly, an Ag/Al_2O_3 catalyst with an AC discharge demonstrated 100% selectivity to CH_4 coupling reactions at 350 °C. Methane coupling using the plasma-catalysis reactor at low temperatures and pressures mainly produced higher hydrocarbons, suggesting a potential route for converting cheap and abundant methane gas into high value hydrocarbons and fuels.

5:20pm **PS+SS-ThA10 Efforts towards Plasma-assisted Catalysis: Elucidating Gas-phase Energetics, Kinetics, and Surface Interactions**, ***Angela Hanna***, *E.R. Fisher,* Colorado State University

With increasing concern about environmental health and climate change, there is a greater need to investigate fundamental reactivity of pollutant species. Improving the effectiveness of substrates used in vehicular emissions abatement hinges on the ability to discern the contributions of gas-phase species in surface reactions. A fundamental understanding of interactions between plasma species is essential to characterizing complex plasma chemistry phenomena. Inductively-coupled N_XO_Y plasma systems were investigated to determine possible synergisms between precursor chemistry and gas-surface interface reactions with a variety of catalytic substrates (i.e., Pt substrates and zeolites). The impact of adding dilute amounts of water vapor to the gas feed was also systematically explored. Precursor chemistry was probed via gas-phase diagnostics; time-resolved optical emission data elucidated NO (g) and N_2(g) production kinetics from N_XO_Y source gases, whereas steady-state emission and absorbance data provide information regarding energy partitioning between rotational and vibrational degrees of freedom. The presence of micro-structured catalysts within the plasma significantly decreases excited N_2 vibrational temperature, suggesting these materials promote vibrational relaxation within the discharge. Our unique Imaging of Radicals Interacting with Surfaces (IRIS) allows us to probe the gas-surface interface and provides evidence of how plasma species synergistically interact with catalytic substrates. In addition to evaluating the spectroscopic characteristics of the discharge (N_XO_Y), we have assessed material morphology and chemical composition before and after plasma exposure. The porous network of zeolite substrates was maintained after prolonged plasma exposure, although surface etching of oxygen or N-doping occurred at different plasma operating conditions. This holistic experimental approach, combining gas-phase diagnostics, IRIS, and robust materials characterization will be essential to realizing the potential of plasma assisted catalysis for pollution remediation.

Thin Films Division
Room A124-125 - Session TF+AS+EL+PS+RA-ThA
Characterization of Thin Film Processes and Properties

Moderators: Richard Vanfleet, Brigham Young University, Virginia Wheeler, U.S. Naval Research Laboratory

2:20pm **TF+AS+EL+PS+RA-ThA1 Phase Separation in III-V Semiconductor Thin Films**, ***Mark Twigg***, *N.A. Mahadik, N.A. Kotulak, S. Tomasulo, M.K. Yakes,* U.S. Naval Research Laboratory **INVITED**

Phase separation in III-V semiconductor alloys remains a problem that limits the performance of electronic materials. As the first stage in a comprehensive program addressing this issue, we have begun investigating an alloy system in which only the group III elements differ: InGaAs. Lattice-matched InGaAs alloy films were deposited at three temperatures (400, 450, and 500C) by molecular beam epitaxy on a (001) InP substrate.

According to kinetic instability theory, the critical temperature for spinodal phase separation in InGaAs is 814C, a temperature well above the growth temperatures used in this study [1,2]. Dark-field (DF) cross-sectional transmission electron microscopy (XTEM), using the composition sensitive g=002 reflection, was used to determine the amplitude of composition modulations averaged over the thickness of the XTEM sample. The amplitude of composition modulation was found to decrease with increasing growth temperature, yielding values of 0.6, 0.4, and 0.3 atomic percent for the growth temperatures 400, 450, and 500C, respectively, a trend in accord with kinetic instability theory. X-ray reflectivity and 2-dimensional small angle x-ray measurements also indicate that the 400C growth shows significantly greater phase separation than the 450 and 500C growths. Atom probe tomography indicates that the amplitude of composition modulation for the 400C growth is approximately 1 atomic percent, a value that compares favorably with the 0.6 atomic percent measured by DF XTEM.

The range of wavelengths for lateral composition modulation is found to extend from approximately 3 to 30 nm. According to the literature, such wavelengths have been found to depend on growth temperature for a number of III-V semiconductor alloys, in agreement with predictions based on surface diffusion. Measurements of the composition modulation wavelength as a function of temperature have been performed by analyzing DF XTEM images recorded using the g=220 diffraction vector, from XTEM samples with the glue line along the rapidly-diffusing [110] direction. Fast Fourier Transform (FFT) power spectra recorded from each image allowed the dominant composition modulation wavelengths to be determined. Analyzing these wavelengths as a function of temperature yields the same activation energy (0.55 eV) as that found in surface diffusion measurements for In adatoms on the (001) InGaAs surface [3]; thereby confirming the role of surface diffusion in phase separation driven composition modulations.

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3:00pm **TF+AS+EL+PS+RA-ThA3 In-Situ Spectroscopic Monitoring of Methylamine-Induced Hybrid Perovskite Phase Transitions**, ***Jonathan Meyers*[1]**, *L.Y. Serafin, J.F. Cahoon,* University of North Carolina at Chapel Hill

Lead halide perovskites have shown remarkable promise for use in thin film optoelectronic devices such as photodetectors, light-emitting diodes, and solar cells. Methods for casting thin films of perovskite have been extensively studied, and great improvements have been made in an effort to improve device efficiency and stability. A few reports have suggested some benefits to processing or post-processing techniques in a methylamine (MA) atmosphere, including healing grain boundary defects to create pinhole free films with grains on the order of tens of microns and improving crystallinity. The process can be observed spectroscopically as the MA induces a reversible phase change which bleaches the dark perovskite film. In this work, we perform the MA-treatment in a vacuum reactor while monitoring in-situ the UV-visible spectral response correlated with temperature and MA partial pressure. Clear evidence is found for the existence of a solid intermediate phase in transitioning from $MAPbI_3$(s) to $MAPbI_3$*xMA(l) and back again. We construct a phase diagram and demonstrate that the critical partial pressure of the phase transition changes from 10 to 500 torr between 25 and 120 °C. By tuning the kinetics of film crystallization, compact films with domains up to 80 µm can be produced.

4:00pm **TF+AS+EL+PS+RA-ThA6 Obtaining Smooth Surfaces and Measuring Surface Roughness**, ***Steven M. George***, University of Colorado at Boulder **INVITED**

Smooth surfaces are important in many areas including friction, adhesion, optics and film growth. Smooth surfaces can be obtained from rough surfaces using chemical mechanical polishing (CMP). Rough surfaces can also be smoothed using atomic layer deposition (ALD) if the conformal ALD film thickness is comparable with the lateral length scale of the roughness. In addition, rough surfaces can be smoothed using isotropic thermal atomic layer etching (ALE) if the ALE etch depth is comparable with the width of the surface asperities. Quantifying the degree of surface roughness after CMP, ALD or ALE is challenging. Surface roughness can be obtained using atomic force microscope (AFM) or x-ray reflectivity (XRR) measurements. However, the AFM and XRR techniques do not always agree. Some of the inconsistencies are attributed to the different lateral length scales for the AFM and XRR measurements. Using both AFM and XRR to characterize surface roughness is recommended for reliable measurements. In addition, XRR measurements for surface roughness should include both specular and diffuse off-specular scattering.

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[1] **National Student Award Finalist**

4:40pm **TF+AS+EL+PS+RA-ThA8 Characterizing Ultra-thin Layer Growth and Area Selective Deposition using High Resolution Low Energy Ion Scattering (LEIS)**, ***Thomas Grehl,*** IONTOF GmbH, Germany; *P. Brüner,* ION-TOF GmbH, Germany; *V. Pesce, B. Pelissier, R. Gassilloud, C. Vallée,* Laboratoire des Technologies de la Microélectronique (LTM), France

When depositing ultra thin films of only very few nm of thickness, the characterization of the early stages of film growth is crucial for the quality of the film. For example, the initial thickness distribution before layer closure, created by the nucleation mechanism, will often remain after the film is complete. To analyze these early stages of growth requires very surface sensitive analytical techniques with good detection limits.

Specifically for area selective deposition, the demand for characterization increases even further. The deposition processes get more complex, involving atomic layer or plasma etching to remove nucleation on blocked areas. This also requires means of characterization, determining the effects of etching steps on the film being created, possible contamination and the level of success of the blocking.

One technique specifically suited for this application is Low Energy Ion Scattering (LEIS). By scattering noble gas ions from the surface of the sample, the mass of the atoms in the outer atomic layer is determined non-destructively. Due to specific charge exchange processes, the peaks in the scattering spectrum correspond only to the outer atomic layer, making LEIS the most surface sensitive technique to determine the elemental composition of a surface.

In addition, information from deeper layers is available in two ways: First of all, features in the spectrum contain information about the first few nm of the sample – especially for heavier elements, the in-depth distribution can be determined non-destructively. For more complex systems or light elements, sputter depth profiling can be applied as well.

In this presentation, we will illustrate the main features of LEIS on ALD films. The main part will be on an area selective deposition (ASD) process for Ta_2O_5 films on TiN or Si. Here, plasma-enhanced ALD (PE-ALD) and various plasma or ALE like etching processes, all using fluorine-containing compounds, are used to develop a super-cycle scheme for ASD. We show the effect of the different etching methods and use sputter depth profiling to determine the distribution of F – a light element not accessible to non-destructive depth profiling in LEIS. An important result is the distribution of F close to the surface, in the bulk of the film, or at the interface.

Besides this, some further sample systems will be used to highlight the use of LEIS for ultra-thin film characterization.

5:00pm **TF+AS+EL+PS+RA-ThA9 Real-Time Monitoring of Aluminum Oxidation Through Wide Band Gap MgF_2 Layers for Protection of Space Mirrors**, *B.I. Johnson, T.G. Avval, G. Hodges, K. Membreno, D.D. Allred,* ***Matthew Linford,*** Brigham Young University

Because of its extraordinary and broad reflectivity, aluminum is the only logical candidate for advanced space mirrors that operate deep into the UV. However, aluminum oxidizes rapidly in the air, and even a small amount of oxide (as little as a nanometer) can have a noticeable, detrimental impact on its reflectivity at short wavelengths. Thin films of wide band gap materials like MgF_2 have previously been used to protect aluminum surfaces. Here we report the first real-time, spectroscopic ellipsometry (SE) study of aluminum oxidation as a function of MgF_2 over layer thickness, which ranged from 0 – 6 nm. SE data analysis was performed vis-à-vis a multilayer optical model that included a thick silicon nitride layer. The optical constants for evaporated aluminum were initially determined using a multi-sample analysis (MSA) of SE data from MgF_2 protected and bare Al surfaces. Two models were then considered for analyzing the real-time data obtained from Al/MgF_2 stacks. The first used the optical constants of aluminum obtained in the MSA with two adjustable parameters: the thicknesses of the aluminum and aluminum oxide layers. The thicknesses obtained from this model showed the expected trends (increasing Al_2O_3 layer thickness and decreasing Al layer thickness with time), but some of the Al_2O_3 thicknesses were unphysical (negative). Because the optical constants of very thin metals films depend strongly on their structures and deposition conditions, a second, more advanced model was employed that fit the optical constants for Al, and also the Al and Al_2O_3 thicknesses, for each data set. In particular, the Al and Al_2O_3 thicknesses and optical constants of Al were determined in an MSA for each of 50 evenly spaced analyses in each four-hour dynamic run performed. The resulting optical constants for Al were then fixed for that sample and the thicknesses of the Al and Al_2O_3 layers were determined. While the first and second models yielded similar Al and Al_2O_3 thickness vs. time trends, the film thicknesses obtained in this manner were more physically reasonable. Thicker MgF_2 layers slow the oxidation rate of aluminum. The results from this work should prove useful in protecting space mirrors prior to launch. Detailed surface/material analysis by X-ray photoelectron spectroscopy will also be shown, as well as more advanced SE modeling.

5:20pm **TF+AS+EL+PS+RA-ThA10 Visualization of Ultrafast Charge Motion in Thin Films via THz Emission Spectroscopy**, ***Aaron Lindenberg,*** Stanford University **INVITED**

We describe a method for probing ultrafast time-dependent currents in thin films and heterostructures by recording the associated emitted electromagnetic fields. This detection scheme offers direct sensitivity to the flow of charges at the atomic-scale and enables a real-time probe for investigating ultrafast charge transfer processes at molecular interfaces. Applied to transition metal dichalcogenide heterostructures having a staggered (Type-II) band alignment, we observe a burst of electromagnetic radiation at terahertz frequencies following above gap excitation. The emitted electric field transients encode information about the charge transfer within the heterostructure. The polarity of the emitted field reflects the direction of the charge transfer and the polarity is reversed as the order of the bilayer within the heterostructure is altered. We find that the charge transfer proceeds at an ultrafast rate (~100 fs) indicating a remarkable efficiency for the charge separation across these atomic-scale bilayers.

We will also describe initial experiments and coupled theoretical efforts probing charge separation and ultrafast photovoltaic responses in multiferroic BFO periodic domain structures. We show that charge separation occurs dominantly at the domain walls and provide a quantitative estimate of the efficiency of this process.

Plasma Science and Technology Division
Room B130 - Session PS+2D+SE+TF-FrM

Plasma Deposition and Plasma-Enhanced Atomic Layer Deposition

Moderators: David Boris, U.S. Naval Research Laboratory, Chenhui Qu, University of Michigan

8:20am **PS+2D+SE+TF-FrM1 Plasma-based Synthesis of 2D Materials for Devices on Flexible Substrates**, *N.R. Glavin,* Air Force Research Laboratory; ***Christopher Muratore,*** Department of Chemical and Materials Engineering, University of Dayton **INVITED**

Synthesis of flexible two-dimensional electronic devices using low-cost, naturally abundant materials (e.g., MoS_2) directly onto inexpensive polymeric materials at economically viable scales enables use of their unique characteristics in grand challenge areas of energy, healthcare, and national security. Recently-proven approaches for low temperature, plasma-based 2D synthesis suitable for flexible substrates developed by the authors include growth of amorphous materials with subsequent photonic annealing to access crystalline domain sizes up to several microns. This approach has been demonstrated for synthesis of large area ultrathin monolithic layers as well as MoS_2/WS_2/BN multilayers with pristine interfaces, allowing interrogation of intrinsic properties of 2D materials and their heterostructures as they apply to diverse optoelectronic devices, with a current focus on molecular sensing. Advantages of plasma-based approaches will be discussed in terms of detailed kinetic studies of crystal formation and compositional evolution on the substrate surface. Correlations of structure, especially defect densities, to materials properties and device performance will be discussed in the context of diverse device applications including photodetectors and molecular sensors.

9:00am **PS+2D+SE+TF-FrM3 Homogeneous Ternary Oxides of Aluminum with Silicon, Molybdenum, and Niobium by Plasma Enhanced ALD by Sequential Precursor Pulses**, ***Steven Vitale,*** MIT Lincoln Laboratory

Deposition of ternary oxide films by ALD is well known. In the vast majority of cases ternary films are deposited by sequential deposition of thin layers of the constituent binary oxides, such as Al_2O_3 / SiO_2. This nanolaminate approach allows for precise control of the global film stoichiometry and is a good solution for many applications, including optical coatings where the wavelength of light is much greater than the nanolaminate thickness thus the film appears quasi-uniform. The nanolaminate approach is less desirable for electronic applications which are sensitive to surface defect sites in the material which may acts as charge traps. For these applications a truly homogenous film which does not possess internal interface states is preferred. True homogenous ternary oxide growth by sequential precursor pulses before the oxidation step is much less well explored. In this work we grow homogeneous ternary oxides of $Al_xSi_yO_z$, $Al_xNb_yO_z$, $Al_xMo_yO_z$ by plasma enhanced ALD using sequential precursor pulses. The stoichiometry of the films is measured by XPS. Using this data we propose models of how the precursors interact with the surface under competitive adsorption. It is found that trimethyl aluminum (TMA) is so strongly adsorbed to the surface at unity surface coverage that ternary oxide growth is not possible if the surface is first exposed to TMA. However if the surface is exposed to the Si, Nb, or Mo precursor first, ternary oxide growth is achieved. The growth kinetics for the three films are markedly different, however, and we explain this through models of the adsorption energy of each precursor.

9:20am **PS+2D+SE+TF-FrM4 Piezoelectric Response of ZnO Thin Films Grown by Plasma-Enhanced Atomic Layer Deposition**, ***Julian Pilz,*** *T. Abu Ali,* Graz University of Technology, Austria; *P. Schäffner, B. Stadlober,* Joanneum Research Forschungsgesellschaft mbH, Austria; *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. Especially the utilization of piezoelectric properties of ZnO nanostructures for transforming mechanical to electrical energy has attracted much research interest. For most of these so called nanogenerators, solution based deposition methods have been applied to create the desired nanostructures, often lacking a precise control of the deposition parameters. Atomic layer deposition, on the other hand, allows conformal and uniform deposition on high aspect ratio structures with Å-level thickness control.

In this study, we investigate the piezoelectric response of ZnO thin films on flexible substrates as a starting point for piezoelectric nanostructures. The films are grown by plasma-enhanced atomic layer deposition (PE-ALD) to thicknesses below 100 nm by adapting diethylzinc and O_2-plasma as reactants. In comparison to thermal ALD (where diethylzinc and water are used as reactants), PE-ALD allows the deposition of films with higher resistivity, an important property to minimize the leakage of piezoelectric charges. Commercially available Polyethylenterephthalat (PET) coated with Indium Tin Oxide (ITO) serves as the flexible substrate and bottom electrode, respectively. The deposition of ZnO thin films is carried out at substrate temperatures between room temperature and 100 °C, as a change in preferential crystal orientation from (100) to (002) can be observed in this temperature range. The macroscopic piezoelectric characterization is performed in a home-built stamp station, in which a defined periodic force is exerted onto the samples and the generated piezoelectric charges are measured. Out of this, the longitudinal piezoelectric coefficient d_{33} can be obtained. Preliminary results show d_{33} coefficients > 7 pC/N, which is comparable to literature results. The piezoelectric characterization is made for the different samples to understand how the d_{33} coefficient changes for films deposited at different substrate temperatures and thus having different crystal orientation. Since the [002] is the polar axis in the ZnO wurtzite crystal structure, films with preferred orientation in this direction are therefore expected to show higher d_{33} coefficients.

The work lays the basis for developing functional piezoelectric generators and sensors in thin film form. However, the concepts can be easily transferred to depositions on lithographically defined templates in order to create nanostructured ZnO, which exhibits increased piezo response.

10:00am **PS+2D+SE+TF-FrM6 Plasma-enhanced Molecular Layer Deposition of Boron Carbide from Carboranes**, ***Michelle M. Paquette,*** *R. Thapa, L. Dorsett, R. Bale, S. Malik, D. Bailey, A.N. Caruso,* University of Missouri-Kansas City; *J.D. Bielefeld, S.W. King,* Intel Corporation

Atomic layer deposition (ALD) research has exploded in this era of electronic miniaturization, smart materials, and nanomanufacturing. To live up to its potential, however, ALD must be adaptable to many types of materials growth. To extend the reach of this layer-by-layer deposition framework, researchers have begun to explore molecule based processes. Still relatively rare, existing molecular layer deposition (MLD) processes are limited and typically based on the condensation of "linear" 2D or "brush-type" organic polymer chains. To this end, icosahedral carborane ($C_2B_{10}H_{12}$) molecules provide an interesting target. Carboranes have been used in the plasma-enhanced chemical vapor deposition of boron carbide films for low-*k* interlayer dielectrics, neutron detection, and a variety of protective coatings. These are symmetric twelve-vertex molecules, known to form close-packed monolayers and to possess labile H atoms at each of the vertices capable of cross-linking in the presence of heat, plasma, or other energy source. As such, the carborane molecule is particularly intriguing as a novel MLD precursor for 3D growth, possessing unique symmetry, reactivity, and volatility properties not commonly encountered in traditional organic molecules. However, a challenge in developing a layer-by-layer process lies in achieving the selective coupling chemistry required, which in the case of molecular reagents requires typically exotic bis-functional derivatives. Herein we describe progress in developing a plasma-enhanced molecular layer deposition process based on carborane derivatives, where the plasma is exploited to create the surface functionalization necessary for selective coupling and to cross-link carborane layers. We investigate the deposition of several carborane derivatives on different functionalized surfaces with the application of various types of plasmas toward achieving controlled layer-by-layer growth of thin boron carbide films.

10:20am **PS+2D+SE+TF-FrM7 Gas Phase Kinetics Optimization Study for Scaling-up Atmospheric Pressure Plasma Enhanced Spatial ALD**, ***Yves Creyghton,*** Holst Centre / TNO, The Netherlands, Netherlands

DBD plasma sources have been successfully integrated in spatial ALD equipment for low-temperature ALD (<120 °C) of metal-oxides. Applications involving (semi)conductive substrates require remote plasma operation. Radical losses during transport from remote plasma limit substrate speeds or demand excessive plasma flow rates. Proximity remote plasma sources were developed with sufficient radical flux even at low gas flow rates. The sources were demonstrated for ALD of InZnO for high mobility thin film transistors. Further optimization asks for deeper understanding of radical kinetics. In this contribution experimental and calculated data will be presented which allow insight in the radical gain and

loss processes. A reference temperature of 100 °C and gas flows in the range 2-10 slm (for a 4 cm wide source) were applied. Alumina depositions were carried out using TMA and 2% O_2-N_2 plasma gas. Deposited layers obtained for different relative height positions of the plasma source were analyzed. Growth per cycle (GPC) values indicate a strong decay of plasma reactivity for gaps > 0.5 mm. As O_3 --should not decay over such small distance, this indicates that the process is radical based. Surprisingly the GPC also shows a peak value at 0.1 mm (Fig. 1). O_3 and NO_x were measured in the plasma exhaust gas as a function of % O_2 (Fig. 2). The 1-2% O_2 for maximum NO appears to correspond with the optimal gas composition for both high GPC values and refractive index values close to 1.58 indicating high layer quality. This result suggests NO plays a role in downstream plasma radical formation. Further understanding of the role of plasma species such as N, metastable N_2(A) and NO has been obtained by modelling. Kinetic data sets for optimization of O_3 production have been implemented in a CFD model for the transport of plasma species from the remote plasma. For the analysis of modelling results, the reaction volume has been divided in 3 parts (1) the plasma ionization zone itself, (2) the flow dominated plasma source aperture and (3) the diffusional transport dominated surface reaction zone. The dominating reactions for gain and loss of O radicals differ much between zones (Fig. 3). As the main O radical formation in zone (2) is due to metastable excited N_2(A), in zone (3) reactions between N radicals and NO are the main source of O radical generation. In both zones, the main O radical loss process is due to generation of O_3. The experimentally validated model has been used for finding improved plasma process settings (source geometry, frequency, flow) allowing the further optimization of high-throughput plasma enhanced spatial ALD of metal oxides.

10:40am **PS+2D+SE+TF-FrM8 Taking Plasma ALD to the Next Level: From Fundamental Understanding to Selective 3D Processing**, *T.F. Faraz, K. Arts,* Eindhoven University of Technology, The Netherlands, Netherlands*; L. Martini, R. Engeln, H.C.M. Knoops,* Eindhoven University of Technology, The Netherlands*; **Erwin Kessels**,* Eindhoven University of Technology, The Netherlands, Netherlands **INVITED**

Current trends in semiconductor device manufacturing impose extremely stringent requirements on nanoscale processing techniques, both in terms of accurately controlling material properties and in terms of precisely controlling nanometer dimensions. Plasma-based processing remains key in next-generation device manufacturing with plasma-enhanced atomic layer deposition (PE-ALD or plasma ALD) being a method that has obtained a very prominent position in obtaining ultrathin films with atomic scale precision [1]. In this contribution the state-of-the-art of PE-ALD will be presented including latest insights into reaction mechanisms as well as some developments in plasma ALD equipment and emerging applications. Aspects such as the role of (energetic) ions, conformality in high aspect ratio structures, and selective processing will be discussed [2].

[1] H.C.M. Knoops, T. Faraz, K. Arts, and W.M.M. Kessels, J. Vac. Sci. Technol. A 37, 030902 (2019)

[2] T. Faraz, K. Arts, S. Karwal, H.C.M. Knoops, and W.M.M. Kessels, Plasma Sources Sci. Technol. 28, 024002 (2019).

11:20am **PS+2D+SE+TF-FrM10 Computational Investigation of Plasma Enhanced ALD of SiO_2**, *C. Qu,* University of Michigan*; P. Agarwal, Y. Sakiyama, A. LaVoie,* Lam Research Corporation*; **Mark J. Kushner**,* University of Michigan

Plasma enhanced atomic layer deposition (PE- ALD) of dielectric films typically consists of two steps – precursor deposition and oxidation. For example, in a SiO_2 PE-ALD process, the Si-containing precursor is often deposited in the feature without use of plasma while the oxidation step is performed by an oxygen containing plasma. In principle, the surface kinetics of both steps are self-terminating. Although the plasma step is performed using gas pressures of several to 10 Torr, in addition to O-atoms the fluxes onto the wafer contain energetic particles in the form of ions, photons, hot-neutrals and excited states. When performing PE-ALD in high aspect ratio (HAR) features, transport of these species into the feature determine the quality of the deposition. Optimizing the PE-ALD depends on control of these fluxes.

In this work, results from a computational investigation of reactor and feature scale processes in idealized PE-ALD of SiO_2 will be discussed. Reactor scale simulations of a capacitively coupled plasma sustained in Ar/O_2 mixtures were performed using the Hybrid Plasma Equipment Model (HPEM); and provided fluxes and energy distributions of radicals, ions, excited states and photons onto the wafer. Feature scale simulations were performed with the Monte Carlo Feature Profile Model (MCFPM). The idealized ALD process consists of a non-plasma first step using an Si-R (R indicates organic) precursor. The second step uses fluxes from the Ar/O_2 plasma to remove the organic and oxidize the Si site. The base-case features are moderate to high aspect ratio (AR = 7-20) vias and trenches. The metrics to evaluate the process are surface coverage of Si, O, R, stoichiometry, defect density, surface roughness and deposition rate.

In self-terminating processes, many of these metrics should scale with pt, where p is the probability of reaction and t is the step length. For example, a given surface coverage of Si-R or Si-O should depend on first order on pt. However, as deposition proceeds and a feature fills, the effective AR increases. When coupled with conductance limited transport into the feature, with increasing AR the value of pt to produce a given surface coverage increases. As the deposition proceeds and AR increases, stoichiometry and defect density begins to have a dependence on height inside the feature, as surfaces deep in the feature receive less exposure to the reactive fluxes. The consequences of ion- and photon-induced damages will also be discussed.

* Work supported by LAM Research Corp. and the DOE Office of Fusion Energy Science.

11:40am **PS+2D+SE+TF-FrM11 Analyzing Self-limiting Surface Reaction Mechanisms of Metal Alkyl Precursors and Nitrogen Plasma Species: Real-time In-situ Ellipsometric Monitoring of III-nitride Plasma-ALD Processes**, ***Ali Okyay***, OkyayTech Inc., Turkey*; A. Mohammad, D. Shukla, S. Ilhom,* University of Connecticut*; B. Johs,* Film Sense LLC*; B.G. Willis, N. Biyikli,* University of Connecticut

ALD-grown films are vastly characterized via ex-situ measurements to quantify various material properties. However, gaining insight into the saturating surface reactions and growth mechanisms is only possible with real-time in-situ process monitoring of individual ALD cycles. While several in-situ measurement techniques have been employed in ALD research, in-situ ellipsometry stands out as one of the best options for real-time monitoring surface reactions. The promising potential of in-situ spectroscopic ellipsometry has already been demonstrated for a number of materials grown by remote plasma-ALD. Here, we verify that cost-effective multi-wavelength ellipsometer (MWE) can also be used effectively for real-time in-situ analysis of plasma-ALD growth cycles. We demonstrate for the first time that real-time dynamic in-situ MWE measurements convey not only accurate film deposition rate, but as well resolve single chemisorption, ligand removal, and nitrogen incorporation events with remarkable clarity. Moreover, forcing the limits for fitting the acquired in-situ MWE data, we were able to track the evolution of the optical constants of III-nitride films along the ALD cycles which indeed showed thickness-dependent behavior.

Our main motivation behind this study was twofold: (i) Analyze and compare the self-limiting growth characteristics of binary III-nitride (AlN, GaN, and InN) thin films via real-time in-situ ellipsometry and to gain insight into the ALD surface reaction mechanisms including chemical adsorption, ligand removal, and nitrogen incorporation steps. (ii) Performance evaluation of our custom designed ALD reactor featuring improved hollow-cathode plasma source by comparing our results with previous plasma-ALD grown III-nitrides.

Despite using the conventional alkyl metal precursors (trimethyaluminum, trimethyl/ethylgallium, trimethylindium) utilized also widely in MOCVD epitaxial growth, their solid-gas surface interactions with nitrogen plasma species shows notable differences, particularly with respect to substrate temperature, plasma power, plasma exposure time, and plasma gas composition. In terms of substrate temperature, AlN exhibited crystallinity at lower temperatures when compared to GaN and InN. Even at 100 °C, AlN showed crystalline behavior whereas GaN displayed amorphous character up to 200 °C. While $Ar/N_2/H_2$ composition is optimal for AlN, N_2/H_2 and Ar/N_2 mixtures proved to be better for GaN and InN. InN experiments revealed that the inclusion of H_2 gas led to mixed phase growth with substantial c-In_2O_3 phase. The possible surface reaction mechanisms that lead to these different growth behaviors will be discussed in detail.

12:00pm **PS+2D+SE+TF-FrM12 Tribological Properties of Plasma Enhanced Atomic Layer Deposition TiMoN with Substrate Bias**, ***Mark Sowa**,* Veeco ALD*; A.C. Kozen,* University of Maryland*; N.C. Strandwitz, T.F. Babuska, B.A. Krick,* Lehigh University

In our previous study, we demonstrated a tertiary plasma enhanced atomic layer deposited transition metal nitride (TiVN) with exceptional wear rates and friction coefficients. We have extended that work with an investigation of another tertiary transition metal nitride system, $Ti_xMo_yN_z$. For films deposited at 250°C and 300W on a Veeco CNT G2 Fiji PEALD system, we have demonstrated how the ratio of TiN:MoN cycles (1:0, 2:1, 1:1, 1:2, 0:1)

provides linear control of the Ti:Mo in the resulting film. Through application of an 13.56MHz RF substrate bias (0-188V) during the plasma step, ion bombardment energy of the substrate can be varied, providing a means for tweaking the films physical and chemical characteristics which in turn are shown to impact the resulting film's tribological properties. As PEALD metal nitrides have broader interest than wear layers and to gain insights on the interrelationships of the mechanical properties, the processing details, and other film properties, we also report on the resulting film composition/impurities, density, crystallinity, optical properties, resistivity, and morphology.

Surface Science Division
Room A220-221 - Session SS+HC+PS-FrM
Planetary, Ambient, and Operando Environments

Moderators: Catherine Dukes, University of Virginia, Petra Reinke, University of Virginia

8:20am **SS+HC+PS-FrM1 Seeing is Believing: Atomic-scale Imaging of Catalysts under Reaction Conditions***, **Irene Groot,*** Leiden University, The Netherlands, Netherlands **INVITED**

The atomic-scale structure of a catalyst under reaction conditions determines its activity, selectivity, and stability. Recently it has become clear that essential differences can exist between the behavior of catalysts under industrial conditions (high pressure and temperature) and the (ultra)high vacuum conditions of traditional laboratory experiments. Differences in structure, composition, reaction mechanism, activity, and selectivity have been observed. These observations indicated the presence of the so-called pressure gap, and made it clear that meaningful results can only be obtained at high pressures and temperatures. However, most of the techniques traditionally used to study catalysts and their reactions were designed to operate under (ultra)high vacuum conditions. To bridge the pressure gap, the last years have seen a tremendous effort in designing new instruments and adapting existing ones to be able to investigate catalysts in situ under industrially relevant conditions.

In this talk, I will give an overview of the in situ imaging techniques we use to study the structure of model catalysts under industrial conditions of atmospheric pressures and elevated temperatures. We have developed set-ups that combine an ultrahigh vacuum environment for model catalyst preparation and characterization with a high-pressure flow reactor cell, integrated with either a scanning tunneling microscope or an atomic force microscope. With these set-ups we are able to perform atomic-scale investigations of well-defined model catalysts under industrial conditions. Additionally, we combine the structural information from scanning probe microscopy with time-resolved mass spectrometry measurements on the gas mixture that leaves the reactor. In this way, we can correlate structural changes of the catalyst due to the gas composition with its catalytic performance. Furthermore, we use other in situ imaging techniques such as transmission electron microscopy, surface X-ray diffraction, and optical microscopy, all combined with mass spectrometry.

This talk highlights a short overview of the instruments we developed and illustrates their performance with results obtained for different model catalysts and reactions. Results for reactions such as NO oxidation and hydrodesulfurization will be discussed.

9:00am **SS+HC+PS-FrM3 *Operando* NAP-XPS and NAP-STM Investigation of CO Oxidation on CoO Nanoislands on Noble Metal Surfaces***, **Jonathan Rodríguez-Fernández**, Z. Sun, E. Rattigan,* Aarhus University, Denmark*; C. Martín, E. Carrasco,* IMDEA Nanoscience, Spain*; E. Pellegrin, C. Escudero,* ALBA Synchrotron Light Source, Spain*; D. Ecija,* IMDEA Nanoscience, Spain*; J.V. Lauritsen,* Aarhus University, Denmark

Nanostructured cobalt oxides (CoOx) have proven to be interesting low temperature oxidation catalysts, for example for preferential oxidation (PROX) of carbon monoxide (CO). CoOx has been identified as one of the most active materials for CO oxidation showing activity down to temperatures as low as –80^{0}C[1]. However, the pure oxide catalyst seems to be strongly poisoned by water. Some studies indicate that combining CoOx with gold synergistically improves the catalytic performance and poisoning resistance[2-3], but an understanding of this metal-oxide effect is lacking. To obtain an atomic scale understanding of the improved catalytic performance of combined Au-CoOx catalysts we have designed a model system where cobalt oxide nanoparticles are synthesized on an Au single crystal surface by physical vapor deposition in an oxygen environment [4-5].

Here, we significantly advance the mechanistic understanding of cobalt oxide nanocatalysts for CO oxidation by studying the surface chemistry of the model catalyst under *operando* conditions. We use powerful near ambient pressure techniques such as scanning tunneling microscopy (NAP-STM) and synchrotron X-ray photoelectron spectroscopy (NAP-XPS) to study CoO_x nanoislands on Au(111) at mbar pressure in a CO/O_2 gas mixture. From STM results, we find that the structure of the ~20nm wide monolayer cobalt oxide nanoislands is static during exposure to a mixture of CO and O_2 gases at a pressure of 1.5 mbar. Under these conditions at room temperature, the nanoislands seem to exhibit activity towards CO oxidation, and we can detect CO, CO_2 surface species by NAP-STM experiments and by analysis of the corresponding O1s and C1s core level NAP-XPS spectra. In addition, we study the morphological evolution by NAP-STM and the reactivity of the CoO nanoislands from RT to 300^{0}C under *operando* conditions. At around 200^{0}C, CO_2 is found in gas phase and decreasing at the surface. Furthermore, to observe the influence of the substrate, we repeated the CoO nanoislands on Pt(111), obtaining similar reactivity results.

References:

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9:20am **SS+HC+PS-FrM4 Reaction of 2-Propanol on SnO_2(110) Studied with Ambient-Pressure X-ray Photoelectron Spectroscopy***, J.T. Diulus, R. Addou,* ***Gregory Herman,*** Oregon State University

Tin dioxide (SnO_2) has a wide range of applications, including gas sensors, transparent conductors, and oxidation catalysts. The surface chemistries for each of these applications can be strongly influenced by the surface structure and cation oxidation states. The oxidation of volatile organic compounds (VOC) has recently been demonstrated using SnO_2, where 2-propanol was used as the probe molecule. More recently it was observed that the surface Sn^{2+}/Sn^{4+}ratio strongly influenced the activity of carbon monoxide oxidation. In this study, we have used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to characterize the surface chemistry of 2-propanol on well-defined SnO_2(110) surfaces. We have prepared stoichiometric and reduced surfaces which were characterized with both AP-XPS and low energy electron diffraction. AP-XPS was performed on these surfaces for 2-propanol pressures up to 1 mbar, various 2-propanol/O_2ratios, and a range of temperatures. These studies allowed us to evaluate the chemical states of 2-propanol on the SnO_2(110) surface under a wide range of experimental conditions. The effect of surface preparation, 2-propanol/O_2ratios, and sample temperature was evaluated using AP-XPS and mass spectrometry. Using valence-band spectra, we have found that the surface was reduced from $Sn^{4+}$to $Sn^{2+}$when the sample was heated in 2-propanol and that the main reaction product in the gas phase was acetone. This suggests that the reaction occurs through a mechanism where bridging oxygens are hydroxylated upon adsorption of 2-propanol. These bridging hydroxyl groups can react and result in water desorption. This process leads to the reduction of the SnO_2(110) surface. We have found that the low temperature AP-XPS spectra (300-400 K) was nearly identical for 2-propanol and 2-propanol/O_2mixtures. After running the reactions at higher temperatures we found that the surface remained oxidized. Several oxidation products were also observed in the gas phase. Based on the experimental results we find that the surface was inactive for the oxidation of 2-propanol for temperatures below 500 K. With 2-propanol/O_2mixtures the reactivity increased substantially at lower temperatures. Furthermore, we propose that in 2-propanol/O_2mixtures the reaction occurs through a Mars–van Krevelen mechanism.

9:40am **SS+HC+PS-FrM5 Chemical Speciation and Structural Evolution of Rhodium and Silver Surfaces with High Oxygen Coverages***, **Daniel Killelea**, M.E. Turano,* Loyola University Chicago*; R.G. Farber, K.D. Gibson, S.J. Sibener,* The University of Chicago*; W. Walkosz,* Lake Forest College*; R.A. Rosenberg,* Argonne National Laboratory

Understanding the interaction of oxygen with transition metal surfaces is important in many areas including corrosion and catalysis. Of interest to us is the formation and chemistry of subsurface oxygen (O_{sub}); oxygen atoms dissolved in the near-surface region of catalytically active metals. The goal of these studies is to understand how incorporation of O_{sub}into the selvedge alters the surface structure and chemistry. The oxygen – Ag system, in particular, has been studied extensively both experimentally and

theoretically because of its role in two important heterogeneously catalyzed industrial reactions: the epoxidation of ethylene to produce ethylene oxide and the partial oxidation of methanol to produce formaldehyde. In addition, the O/Rh and O/Ag systems serve as models for the dissociative chemisorption of diatomic molecules on close packed metal surfaces. Despite extensive research, there remain questions about the fundamental chemistry of the O/Ag system. Rh is also used in partial oxidation reactions, and its response to adsorbed oxygen provides an interesting complement to Ag. Where Ag extensively reconstructs, Rh does not. In particular, the structure of the catalytically active surface remains poorly understood under conditions of high oxygen coverages or subsurface oxygen. To improve our understanding of this system, we use ultra-high vacuum (UHV) surface science techniques to characterize Ag and Rh surfaces after exposure to atomic oxygen (AO) to obtain O coverages in excess of 1 ML. AO is generated by thermally cracking molecular O_2. We then use low-energy electron diffraction (LEED) and UHV Scanning Tunneling Microscopy (UHV-STM) to further characterize the various oxygenaceous structures produced, and quantify the amount of oxygen with temperature programmed desorption (TPD). We have found that the surface temperature during deposition is an important factor for the formation of $O_{sub}$and the consequent surface structures. Finally, we have recently found that Rh surfaces are significantly more reactive towards CO oxidation when O_{sub} is present. This enhanced reactivity is located at the interface between the less reactive RhO_2oxide and O-covered metallic Rh. These results reveal the conditions under which $O_{sub}$is formed and stable, and show that O_{sub}also leads to enhanced reactivity of oxidized metal surfaces.

10:00am **SS+HC+PS-FrM6 Molecular Processes on Icy Surfaces in the Interstellar Medium and the Outer Solar System*, Edith Fayolle*,** *R. Hodyss, P. Johnson,* Jet Propulsion Laboratory, California Institute of Technology*; K. Oberg,* Harvard University*; J-H. Fillion, M. Bertin,* Sorbonne Université **INVITED**

Molecular ices have been observed in various planetary and astrophysical environments: from patches in permanently shadowed regions on Mercury and the Moon, to the ice crust of outer Solar System bodies, and onto dust grains in prestellar cores, protostellar envelopes, and protoplanetary disks. Interstellar and planetary ices are mostly composed of H_2O, and more volatile molecules, e.g. N_2, CO, CH_4, CO_2, H_2S, SO_2, NH_3, held together as a solid through van Der Waals forces and dipole-dipole interactions, such as hydrogen bonding. They are found as mixtures or pure layers and display crystalline or amorphous structures.

Understanding ice formation, sublimation, and composition is crucial to interpret both gas phase and solid state observations, constrain the physical conditions encountered in space, and test for the likely chemical inheritance from star-forming environments to planetary systems. Vacuum and cryogenic techniques are used to reproduce astrophysical conditions and grow ice analogues. Analytical techniques, including IR- UV-spectroscopy, mass spectrometry, and microgravimetry, are employed to measure fundamental parameters such as desorption, diffusion energies, and reactions products & rates in the solid phase.

In this talk, I will show several examples of astrochemical experiments relevant to icy environments. The fundamental parameters derived from these experiments are further used as inputs for astrochemical models simulating the formation and evolution of ices on various bodies. In some cases, these experiments can directly explain recent observations, for e.g., the unexpected variety of molecules detected in lunar cold traps by the Lunar Crater Observation and Sensing Satellite mission or the location of snowlines in protostellar and protoplanetary environments probed by radio-interferometers like the Atacama Large Millimeter Array.

10:40am **SS+HC+PS-FrM8 Bilayer Silicates as Models for Space-weather-mediated Water-cycling Processes at the Interface of Airless Bodies***, B. Dhar,* ***William E. Kaden,*** University of Central Florida

Following recent observations indicating the presence of water and/or hydroxyl groups inhomogeneously distributed across the surface of the moon, many groups have worked to put forwarded feasible models necessary to rationalize both effects. From those models, there seems to be reasonable agreement that a solar-wind mediated, H^+ implantation-based mechanism is responsible for initial hydration/hydroxylation at the lunar surface. How and why the OH-group concentration varies with both latitude and longitude, however, remains debated in the literature. A recently reported kinetics model provided a plausible temperature-dependent recombinative desorption/dissociative readsorption pathway, which accurately predicts observed systematic trends in the concentration of OH groups as a function of latitude when also accounting for daily oscillations in photon and proton flux vs. latitude over long periods of time. Key to the postulated OH-group migration pathway is the presence of mineral surfaces with atypically low barriers to recombinative water desorption; something that varies with both surface composition/structure and OH group concentration. To account for the effects of the average lunar mineralogical surface composition, the author's simply modeled the moon as a homogenous distribution of simple binary oxides present at concentrations corresponding those associated with each of the corresponding metals.

In the work presented in this this talk, we have used recently developed recipes allowing for the growth of extremely well-defined, atomically-planar, and crystalline silicate sheets to serve as tailor-designed anologues of mineralogically relevant structures containing deliberately varied surface sites expected to be present at the surface of the moon and elsewhere. More specifically, we have grown and fully characterized two bilayer films; one consisting of pure silica (SiO_2) and the other present as a two-dimensional alumino-silicate ($Al_{0.33}Si_{0.67}O_2$). Using temperature programmed desorption, we have then characterized differences in the OH-silicate interactions as a function of one deliberately varied surface-site's coordination, and then link our observations to help provide a more nuanced insight into how and why water may evolve and cycle into and out of the surface of airless bodies in the presence of the solar wind.

11:00am **SS+HC+PS-FrM9 Unraveling the Evolution of the Solid-Electrolyte Interphase Layer at Li-Metal Anodes***, **Venkateshkumar Prabhakaran**, S. Roy, G.E. Johnson,* Pacific Northwest National Laboratory, Joint Center for Energy Storage Research*; M.H. Engelhard, V. Shutthanandan, A. Martinez, S. Thevuthasan,* Pacific Northwest National Laboratory*; K.T. Mueller, V. Murugesan,* Pacific Northwest National Laboratory, Joint Center for Energy Storage Research

Chemical transformations of electrolyte constituents (such as solvent and solvated electroactive ions) at the Li-metal electrode determine the evolution of the solid-electrolyte interphase (SEI). The ability to rationally design an SEI layer that will provide efficient charge transfer processes will improve the performance of Li-batteries. The main challenge is to unravel the complex set of interfacial reactions that occur during charge transfer processes and subsequently delineate the pathways of various decomposition reactions and phase formation. Herein, we report progress in understanding such complex interfaces using bottom-up assembly of solvated cations and bare anions of selected composition on Li-metal anodes. Soft landing of mass-selected ions, a versatile approach to surface modification, is ideally suited for building the interface with selected electroactive ions which will help unravel the complexity associated with the multitude of interfacial processes occurring during evolution of the SEI layer.[1,2] Ion soft landing combined with operando infrared reflection-absorption spectroscopy (IRRAS) and in-situ x-ray photoelectron spectroscopy (XPS) were used to characterize the decomposition of counter anions and solvent molecules on bare Li metal surfaces. Specifically, we soft-landed isolated electrolyte anions (*e.g.,* bis(trifluoromethane)sulfonimide, $TFSI^-$, polysulfides, S_x^-) and solvated Li solvent cluster cations (e.g. Li-(dimethoxyethane)$_x$) on bare Li metal surfaces without their corresponding counter ions, and monitored their spontaneous decomposition using IRRAS and XPS. Our in-situ multimodal measurements captured the spectroscopic signatures of reaction pathways of the electrolyte anions and solvent molecules on the reactive Li surface. We will discuss the evolution of the SEI layer based on multimodal spectroscopic analysis of electrochemical interfaces prepared using the ion soft landing approach. In particular, the chemical signatures of transient species that evolve during decomposition at well-defined interfaces will be discussed.

References:

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