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

Moderator: Jing Xia, University of California Irvine

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

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

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

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

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

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

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

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

References

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

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4. Wang et al., in progress (2018).

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

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

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

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

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

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

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

References:

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

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

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10:00am **2D+EM+MI+NS+TF-MoM6 Synthesis and Characterization of 1T, 1T', and 2H $MoTe_2$ Thin Films**, ***Thomas Empante**,* University of California, Riverside*; Y. Zhou,* Stanford University*; S.A. Naghibi Alvillar,* El Camino College*; E.J. Reed,* Stanford University*; L. Bartels,* University of California, Riverside

Transition metal dichalcogenides (TMDs) have been of interest over the past few decades for their intriguing structural, electronic, and optoelectronic properties, particularly when scaled down to thin films. One of the most interesting TMD materials is molybdenum ditelluride ($MoTe_2$) because of its relative ease to attain multiple phases at room temperature, namely the metallic 1T' phase and the semiconducting 2H phase. Here we show a facile chemical vapor deposition process to synthesis not only the aforementioned phases but the elusive unreconstructed 1T phase by regulating the cooling rate and the addition of carbon dioxide during the reaction. Our experimental Raman spectroscopy results were compared to theoretical density functional theory calculations which verify the synthesis of all three phases. Electronic transport measurements were also used to characterize the films and show that the newly synthesized 1T phase is in good agreement with theoretical models depicting semi-metallicity as the material shows increased conductivity with elevated temperatures. In addition to the pure phase materials, mixed phase materials, such as 2H/1T, can be synthesized with slight alterations to the parameters leading to enhancements of the 2H phases' conductivity.

11:20am **2D+EM+MI+NS+TF-MoM10 Low-Defect, High-Uniformity Transfer-Free Graphene on SiO_2 by Thermal Chemical Vapor Deposition**, ***Leslie Chan**, D.S. Tsai, Z. Wang, C. Carraro, R. Maboudian,* University of California, Berkeley

Chemical vapor deposition (CVD) has emerged as the customary approach for scalable, controllable production of graphene for integrated devices. Standard CVD graphene must be transferred from a generic metal growth substrate onto the desired substrate (*e.g.*, SiO_2), but this extra transfer often leads to wrinkles, contamination, and breakage that ultimately result in poor device performance. Several groups have demonstrated metal-catalyzed direct CVD-graphene growth on insulating substrates, but the final graphene products are deficient in quality and uniformity. This work details an expansion of the parameter space that enables lower-defect, higher-uniformity graphene than previously reported using nickel and copper catalysts, respectively. We introduce a mechanism based on carbon permeability that provides deeper insight into the growth process. Ultimately, these studies seek to inform the judicious choice of process parameters that will lead to large-area, high-quality, layer-controlled graphene directly on target substrates.

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

Plasma Deposition and Plasma-Enhanced ALD

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

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

Partially stabilized zirconia is widely used in thermal barrier coatings that requires a thermodynamically stable and highly durable interface with a natively grown aluminum oxide (Al_2O_3) scale. The potential of ZrO_{-2} to serve as an effective Thermal barrier coating (TBC) has already been demonstrated along with modest corrosion resistance. The ECAP experiment (Evaporative Coatings at Atmosphere Pressure) was developed at CPMI (Center for Plasma Materials Interaction at UIUC) as a device for surface treatment at atmosphere pressure utilizing a 2.45 GHz microwave plasma torch. Recent modifications to this system allows for delivery of precursors and target materials through the torch that gives it the capability to deposit thin films. The goal of this study is to compare the quality of the ZrO_{-2} films grown using each of these methods. Various methods will be used to characterize the quality of films grown including Nanoindentation, XPS, XRD and Profilometry.

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

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

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

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

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

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

Wood components have been used as a building material for centuries. In light of the growing concern over the environmental impact of human industrial activity, wood has taken on a new importance worldwide. The main advantages of this widely-distributed and renewable resource lie in its versatility, strength-to-weight characteristics, ease of processing, aesthetics, and its sustainability as a green-material. Its bio-polymeric structure, however, renders it susceptible to degradation due to moisture, microorganisms, insects, fire, and ultraviolet radiation. In this context, important research efforts have been devoted to the further development of existing wood protection systems either through the application of paints, varnishes, stains, and water repellents or through direct modification by thermal, chemical, and impregnation methods. In recent years, we have shown that non-thermal plasmas represent a very promising approach for tailoring the surface properties of wood-based materials for both improvement of existing protection systems or as standalone treatment for the growth of functional coatings. In this presentation, the scientific and technological accomplishments associated with the use of plane-to-plane dielectric barrier discharges at atmospheric pressure for plasma-enhanced chemical vapor deposition (PECVD) of various barrier coatings on wood surfaces are reviewed. These aspects

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

cover the effects of wood conditions and properties, such as wood inhomogeneities and wood outgassing, on both the plasma characteristics and the plasma deposition dynamics of SiOCH barrier layers using organosilicon precursors. This description is extended to more complex systems such as the plasma-assisted growth of nanocomposite coatings (for example TiO2 or ZnO nanoparticles embedded into a SiOCH matrix) using colloidal solutions as the growth precursor for PECVD. For such applications, a combined low-frequency-high-frequency voltage waveform is used to achieve significant and spatially uniform deposition of nanoparticles across the whole substrate surface. Finally, very recent studies on the plasma-assisted functionalization of highly porous microfibrillated cellulose materials derived from the wood biomass are presented.

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

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

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

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

In this work, we will discuss characterization of a reactor that imitates an industrial PEALD tool using experimental and computational investigations. The system is flowing afterglow geometry, where a barrel-type ICP source is mounted on one side of the reactor and produces a plasma that expands into a chamber with access ports to diagnose the plasma properties using optical emission spectroscopy and charged particle flux probes. The computational model is based on a multi-species, two-temperature fluid description of plasma with finite rate chemistry. Results will be discussed in Ar and Ar/N_2 plasmas over varying pressure and inductive power with particular emphasis on the impact of N_2 addition on plasma properties and the chemical composition of radicals incident on the wafer.

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

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

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

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

In this study, we investigated the effect of substrate temperature in the range 25 °C – 250 °C on the ZnO material properties. The films were grown by direct PE-ALD adapting diethylzinc and O_2-plasma as reactants. By adjusting the substrate temperature, it was possible to switch the texture of the films from (100) at room temperature to (002) above 150 °C. The growth per cycle (obtained by spectroscopic ellipsometry, SE) ranged from 1.6 to 4.0 Å/cycle, suggesting a temperature dependent growth behavior. Further SE analysis showed a range of refractive index (at 633 nm) from 1.87 to 1.94 and a bandgap range of 3.255 to 3.270 eV. X-ray photoelectron spectroscopy survey scans pointed out a non-detectable carbon content and a O/Zn ratio of around 1.17 (constant over the whole temperature range), while high-resolution scans of the O1s-peak showed a decrease in OH-content from 21 % (at 25 °C) to 9 % (at 250 °C). Further analysis will focus on resistivity (and its relation to OH-content), transparency, and piezoresponse.

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

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

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

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

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

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

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

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

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

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

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

We are working on the development of a discharge source using tailored waveforms for plasma enhanced atomic layer deposition (PEALD) processes. The discharge sources employed in this study are 13.56 MHz RF, pulsed DC or their combination [1], and their applicability to PEALD process of titanium dioxide (TiO_2) thin films has been evaluated. A titanium precursor adsorbed on a silicon substrate having amorphous carbon (a-C) patterns is oxidized by applying these discharges in argon/oxygen mixtures. Thus PEALD process of TiO_2 films is achieved accordingly. The experimental results obtained from scanning transmission electron microscope show that TiO_2 films are deposited with excellent step coverage independent of the discharge sources. However, the film characteristics at each deposition position of a-C patterns (i.e. at the top, side and bottom) greatly vary depending on the discharge sources, which has been confirmed by the evaluation of the wet etching rate using a diluted hydrogen fluoride solution. The clear variation of the film characteristics is presumably attributed to the change in the number density of reactive species (electrons, ions, radicals), their ratio and the ion angle distributions, all of which are determined by the discharge sources.

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

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

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

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

Nanostructured Thin Films and Coatings

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

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

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

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

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

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

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

It is generally believed that single-crystalline substrates with either the bulk or surface structure and lattice constant identical or similar to that of the film being deposited are required for the growth of high-quality crystalline thin films. Recent studies have shown that deposition on van der Waals (vdW) layers can lead to highly-oriented thin films of a variety of crystal structures and lattice parameters. Here, we show that two-dimensional (2D) hexagonal boron nitride (hBN) layers (a = 0.250 nm and c = 0.667 nm) improve the crystallinity of trigonal-structured Ta_2C (a = 0.310 nm and c = 0.494 nm) thin films sputter-deposited on $Al_2O_3(0001)$ substrates. Ta_2C layers of desired thickness (t = 17 ~ 75 nm) are grown on bare and hBN-covered $Al_2O_3(0001)$ substrates via ultra-high vacuum direct current magnetron sputtering of TaC compound target in 20 mTorr pure Ar gas atmospheres at 1327 K. hBN layers are deposited via pyrolytic cracking of borazine (~600 L) onto $Al_2O_3(0001)$ substrates at 1327 K. The as-deposited Ta_2C films are characterized *in situ* using Auger electron spectroscopy and low-energy electron diffraction and *ex situ* using X-ray diffraction (XRD) and

transmission electron microscopy (TEM) based techniques. ω-2θ XRD scans acquired from both $Ta_2C/Al_2O_3(0001)$ and $Ta_2C/hBN/Al_2O_3(0001)$ films with t = 17 nm exhibit only Ta_2C 0002n reflections (corresponding to c = 0.494 nm) while thicker layers (t = 75 nm) reveal the presence of additional 10 1 reflections. However, the 0002 reflection peak intensities are 5.4-fold stronger for the Ta_2C layers on $hBN/Al_2O_3(0001)$ than bare $Al_2O_3(0001)$. High-resolution TEM images and associated Fourier transforms indicate that the layers are single-crystalline. XRD ϕ scans show six 60°-rotated 1 0 -1 2 peaks of Ta_2C at the same φ angles for 1 1 -2 6 of Al_2O_3 based on which we determine the epitaxial crystallographic relationships between the film and the substrate as $Ta_2C(0002)$ || $Al_2O_3(0006)$ with in-plane orientation of Ta_2C[1 0 -1 0] || Al_2O_3[1 1 -2 0]. We further show that 0002-oriented Ta_2C thicker films can be obtained by inserting hBN layers at regular intervals during the deposition of thicker Ta_2C films.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Monday Morning, October 22, 2018

Thin Films Division
Room 102A - Session TF1-MoM
Precursors and Surface Reactions

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

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

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

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

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

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

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

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

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

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

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

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

Anhydrous Hydrogen Peroxide Gas

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

[1] **National Student Award Finalist**

High Concentration Hydrogen Peroxide Gas

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Thin Films Division
Room 104B - Session TF2-MoM

IoT Session: Thin Film Processes for Energy Storage

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

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

Lithium-ion batteries have been an enabling factor in the success of consumer electronics and have the potential to offer energy storage solutions for microelectromechanical systems (MEMS). Current thin film battery technology consists of a two-dimensional planar stack of materials characterized by poor volumetric utilization where large areal footprints are required to supply the needed energy and power for device operation. Moving away from these traditional two-dimensional batteries towards next generation three-dimensional battery architectures (e.g. cylindrical arrays, interdigitated plates, etc.) allows for an effective decoupling of the areal energy and power density resulting in improved areal footprint

utilization. In 3D architectures, the short distances between the anode and cathode improve the transport properties allowing for high areal power densities and the high aspect-ratio nature of the electrodes promotes high areal energy densities. Integration with these 3D architectures presents a challenge—requiring the synthesis of conformal thin films of both the electrolyte and counter-electrode, where optimization of the solid electrode/electrolyte interface is crucial for optimal device performance. Cobalt oxide is a potential candidate as a high capacity thin film anode material demonstrating lithiation capacities of 716 and 891 mAh/g for CoO and Co_3O_4, respectively.

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

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

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

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

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

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

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

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

Energy Sciences (Award no. DESC0001160).

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

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

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

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

Over the last decade, the research community engaged in significant efforts to investigate novel anode materials for Li-ion batteries with the goal of increasing the storage capacity of these devices. Among several candidates, silicon-carbon nanocomposites represent one of the most promising choices, featuring the highest theoretical gravimetric storage capacity. The small size of the silicon -Si- structures tackles the volume expansion undergone by the semiconductor upon lithiation, which causes pulverization of bulk Si electrodes, and promotes a robust cycling. The carbonaceous coatings, on the other hand, improve the electrical conductivity of the composite and prevent the direct interaction of Si with the electrolyte which in turn enhances the stability of the solid electrolyte interphase. Although a wide range of different Si-C nanocomposites have been investigated, these structures are often produced with methods characterized by questionable scalability, hence hindering the immediate introduction of these materials into actual manufacturing. In this contribution, we describe a facile and scalable-by-design approach for the fabrication of Si-core graphite-shell nanoparticles -NPs. Commercial Si NPs with an average size of 100 nm are introduced into a hot-wall furnace with an alumina combustion boat. The NPs are wrapped with a conformal coating of amorphous carbon resulting from the dissociation of acetylene -C_2H_2- at 650 °C. After removing C_2H_2 from the reaction zone, the furnace is

ramped up to 1000°C in Argon -Ar- yielding a controlled graphitization of the C-shell, as highlighted by Raman and TEM analysis, with no detectable presence of silicon-carbide. The as-produced composites are introduced into a slurry with no addition of conductive additives, coated onto a copper substrate and studied as pure anode material in Li-ion battery half-cell assemblies. The amorphous-C-coated Si NPs exhibit a high first cycle coulombic efficiency – CE – in the order of 87% and a capacity of 1800 mAh g^{-1} which rapidly decays below 1000 mAh g^{-1} during the first 40 cycles. The graphitization of the C-shell, achieved through the high-temperature step in Ar, significantly improves the cycling stability of the material showing a capacity above 1500 mAh g^{-1} over more than 100 cycles. Finally, the silicon-graphite composite is tested as a simple drop-in additive in graphite anodes. The addition of small amount of the Si-based active material (10% in wt) enables the fabrication of electrodes with a gravimetric capacity 30% higher than the one of the pure graphite electrodes used in commercial batteries, a first cycle CE of 90% and stable cycling over 100 cycles.

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

Moderator: Robert Grubbs, Micron Technology

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

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

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

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

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

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

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

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

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

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

Heusler compounds have received a lot of attention because of their large range of properties. Their properties depend on the number of valence electrons per formula unit and have been predicted to be semiconductors, metals, ferromagnets, antiferromagnets, half metals, superconductors and topological insulators. Similar to compound semiconductors, the band structure and lattice parameters of Heusler alloys can also be tuned through alloying but over a much larger range of properties. Magnetic tunnel junctions using Heusler alloys that are predicted to be half metals have shown record tunneling magnetoresistance. Heusler half metals have been predicted to have very low Gilbert damping coefficients. They can also be lattice matched to most compound semiconductors and have been used for spin injecting contacts. Recent theoretical predictions suggest that atomic level Heusler superlattices can result in half metallicity and perpendicular magnetization. This presentation will emphasize the molecular beam epitaxial growth combined with in-situ and ex-situ structural, electronic and magnetic characterization of Heusler heterostructures on III-V semiconductors and MgO single crystal substrates. Tuning of their magnetic and electronic properties through elemental substitution to change the number of valence electrons per

formula unit and atomic level superlattice growth will be discussed. Examples of Heusler heterostructures and controlling of their magnetic and electronic properties include tuning of the spin polarization in $Co_2Mn_{1-x}Fe_xSi$, Heusler contacts for spin injection into GaAs, spin polarization and magnetic anisotropy of Co_2MnAl/Fe_2MnAl atomic scale superlattices, substitution with Fe in CoTiSb with the aim to convert a semiconductor to half metal and interfacial reactions at Co_2MnSi/MgO interfaces. By careful tuning of the half metallic Heusler film composition, Gilbert damping coefficients <0.001 have been observed.

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

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

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

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

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

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

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

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Thin Films Division
Room 104B - Session TF-MoA
IoT Session: Thin Films for Photovoltaics

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

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

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

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

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

The need for environmentally stable perovskite solar cells (PSCs) has promoted the quest for moisture and thermal stress barrier layers that can adequately seal the perovskite absorber. Atomic layer deposited (ALD) metal oxides are widely acknowledged for their continuous and pinhole-free nature, derived from the self-limiting deposition process. We have recently shown that 10 cycles of ALD Al_2O_3 deposited directly on top of $CH_3NH_3PbI_{3-x}Cl_x$ perovskite are effective in delivering a superior PSC performance with 18% efficiency (compared to 15% of the Al_2O_3-free cell) and long-term humidity-stability of more than 60 days.[1,2] Motivated by these results, the present contribution focuses on the chemical modifications which the $CH_3NH_3PbI_{3-x}Cl_x$ perovskite undergoes upon growth of ALD Al_2O_3. Specifically, we couple *in situ* infrared spectroscopy studies during film growth, with XPS analysis of the ALD Al_2O_3/perovskite interface. The IR-active signature of NH_3^+ stretch mode (asymmetric at 3179 and symmetric at 3132 cm^{-1}) of the perovskite undergoes minimal changes upon exposure to ALD cycles, indicating no diffusion of the ALD precursors (TMA and H_2O) into the bulk of the perovskite. The exclusion of H_2O infiltration is evident also from the absence of two well-defined peaks at 3500 and 3450 cm^{-1}. These conclusions are supported by Doppler broadening-positron annihilation spectroscopy studies, revealing no changes in the open volume of 'bulk' perovskite upon deposition of Al_2O_3. Analysing the differential IR spectra (Absorbance$_{(perovskite + Al2O3)}$-Absorbance$_{(pristine\ perovskite)}$) with increasing ALD cycles, the abstraction of NH_3^+ from the perovskite surface is discerned, with the appearance of negative N-H stretch and bend modes. In parallel, the growth of ALD Al_2O_3 on perovskite is witnessed by the characteristic IR-active Al-O-Al phonon and (OH)-Al=O stretch modes. Based on the XPS analysis, a plausible growth mechanism of ALD Al_2O_3 on top of perovskite is discussed. During the first half- cycle, TMA reacts with perovskite via the interaction of one of its methyl groups with one of the H atoms of $CH_3NH_3^+$ of perovskite. This interaction weakens the hydrogen-bonds between $CH_3NH_3^+$ and I^- of the perovskite, resulting in breakdown of the organic moiety from the inorganic framework. CH_3NH_2 and CH_4 are released as byproducts, leaving behind an adduct comprising of PbI_3-$Al(CH_3)_2$. In the next half-cycle of H_2O dosage, the H_2O molecule can react with the PbI_3-$Al(CH_3)_2$ adduct and generate the –OH surface sites necessary to promote the growth of Al_2O_3.

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

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

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

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

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

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

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

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

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

3:40pm **TF-MoA8 Sulfur Vacancies as the Origin of *n*-type Doping in Pyrite FeS_2 Single Crystals**, *B. Voigt, W. Moore, J. Walter, D. Ray, M. Manno,* University of Minnesota*; J.D. Jeremiason,* Gustavus Adolphus College*; L. Gagliardi,* ***Eray Aydil****, C. Leighton,* University of Minnesota

Pyrite FeS_2 is an ideal photovoltaic material for low-cost and sustainable thin film solar cells because it is composed of earth-abundant, non-toxic, inexpensive elements, has a suitable band gap well-matched to the solar spectrum, and absorbs light so strongly that a 100 nm thick film is adequate to absorb over 90% of all photons with energies above the band gap. While pyrite FeS_2 was pursued vigorously in the 1980's as a potential solar cell material, efficiencies never exceeded 3 %. One of the fundamental problems was a lack of control over doping. Recently, rigorously phase-pure pyrite FeS_2 single crystals and thin films were shown to be exclusively *n*-type, with a universal dependence of electron mobilities in both thin films and crystals on Hall coefficient suggesting that a common dopant is responsible for this *n*-type behavior. This dopant, however, has not been identified. We have amassed the strongest evidence to date that sulfur vacancies are this common dopant. Single crystals with experimentally indistinguishable lattice parameters, mosaic spread, and nominal stoichiometry, grown via chemical vapor transport under different sulfur vapor pressures, show significantly different electron densities and mobilities. Specifically, crystals grown under high sulfur vapor pressure exhibit semiconducting behavior and temperature-dependent electron

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

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

densities with an activation energy of 225 meV. Decreasing the sulfur vapor pressure during crystal growth decreases this activation energy, increases the electron density and mobility, and triggers metal-like conduction observed in temperature-dependent resistivity measurements. This is consistent with higher concentrations of sulfur vacancies in pyrite crystals grown under decreased sulfur vapor pressure. These trends are independent of transition metal impurity concentrations and, importantly, electron densities are too large to be explained by trace amounts of transition metal impurities. All evidence thus implicates sulfur vacancies as the ubiquitous *n*-type dopant in pyrite FeS_2.

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

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

Hybrid perovskite solar cells have attracted tremendous attention due to the low cost and high-power conversion efficiency. The biggest barrier to its commercialization is the poor stability in the outdoor environment.Al_2O_3 atomic layer deposition (ALD) has shown great promise in improving the environmental stability of hybrid perovskites, however, the nucleation of ALD Al_2O_3 on perovskite has not yet been understood, especially the reaction between tri-methyl aluminum (TMA), a strong Lewis acid, and fresh hybrid perovskites. In our work, the growing behavior and surface reaction mechanism of Al_2O_3 ALD (Trimethyl Aluminum (TMA) and H_2O chemistry) on $CH_3NH_3PbI_3$ perovskite is studied systematically by *in situ*quartz crystal microbalance(QCM) and *in situ*quadrupole mass spectrometers (QMS).We find that the reaction temperature is the key parameter affecting the nucleation of Al_2O_3 ALD on $CH_3NH_3PbI_3$. At 25°C, TMA can accumulate mass onto the surface of a fresh $CH_3NH_3PbI_3$ substrate through substrate site-limited reactions. The surface passivation provided by TMA adsorption at 25°C improves the ambient stability of $CH_3NH_3PbI_3$. In contrast, at 75°C, TMA etches $CH_3NH_3PbI_3$ by the formation of volatile products, which will degrade $CH_3NH_3PbI_3$ to PbI_2.

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

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

Thin Films Division
Room 104B - Session TF+AM+EM+PS-TuM
Atomic Layer Processing: Area Selective Deposition

Moderators: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, France, Steven George, University of Colorado at Boulder

8:00am **TF+AM+EM+PS-TuM1 New Approaches for Area-Selective Atomic Layer Deposition: Inspiration from Etching***, **Adrie Mackus,*** Eindhoven University of Technology, The Netherlands, Nederland **INVITED**

While selectivity has always been one of the most important features of an etching process, only in recent years there has been significant interest in selectivity for deposition, motivated by the application of area-selective deposition in self-aligned fabrication. With selective etching being a more mature technology, previous work in etching can serve as inspiration for how to make deposition processes selective. For example, inhibition layers have been employed in etching to obtain selectivity. Similarly, the use of small molecule inhibitors is currently being explored for achieving area-selective atomic layer deposition (ALD).[1]

Moreover, with the recent advancements in atomic layer etching (ALE), new opportunities emerge for selective processing of material based on novel combinations of ALD and ALE. In recent work, ALE cycles have been implemented in area-selective ALD processes to improve the selectivity.[2]

In this presentation, the similarities between etching and area-selective ALD will be described, in order to discuss what the area-selective ALD community can learn from previous work in etching. Recent developments in area-selective ALD will be illustrated by discussing new area-selective ALD approaches based on the use of inhibitors in ABC-type (i.e. three-step) ALD cycles, and on supercycles combining ALD and ALE cycles.

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. R. Vallat, R. Gassiloud, B. Eychenne, and C. Vallée, *J. Vac. Sci. Technol. A.***35**, O1B104 (2017)

8:40am **TF+AM+EM+PS-TuM3 Nucleation of HfO_2 on Si, SiO_2 and TiN Substrates in PE-ALD Processes Investigated by In situ Ellipsometry and Optical Emission Specroscopy (OES)***, **Marceline Bonvalot**, S. belahcen, V. Pesce, A. Chaker, P. Gonon, C. Vallée, A. Bsiesy,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

It is generally admitted that the physical properties of ultrathin layers elaborated by ALD processes are strongly dependent upon the very initial stages of layer growth, defined as the nucleation step. This nucleation step may for instance affect the cristallinity and the texturation of the material when growing in a crystalline state, it can also significantly contribute to the sharpness of the interface between the substrate and the growing material and/or determine the layer density and surface rugosity. Moreover, this nucleation step also plays a major role in the advancement of Selective Area Deposition Processes (SALD), which are considered, as of today, as a very promising approach for the development of bottom-up routes alternative to increasingly expenseive thin layer patterning processes. In these regards, a good knowledge of the phenomena affecting the nucleation mechanisms in ALD is required.

In this work, the initial stages of layer growth has been investigated during the deposition of HfO_2 by Plasma-Enhanced ALD in a FlexAL set-up equipped with an ALE (Atomic Layer Etching) bias system developed by Oxford. Four types of substrates have been put on trial for this purpose, namely, HF last treated Si(100), SiO_2 (45 nm dry oxide)/Si, SiO_2 (500 nm wet oxide)/Si, and TiN (15 nm ALD)/Si. Several in situ surface treatments have been applied on these substrates, prior to HfO_2 ALD cycles with TEMAH as hafnium precursor. They include exposure to a plasma treatment composed of either Ar, CF_4 and O_2 or any mixture of these gases. A very low power (1-10 W) can be applied on the substrate to allow low DC self-bias voltage, which determines energies of ions extracted from the plasma in the vicinity of the substrate. This bias in turn allows an estimation of the contribution of both chemical and physical plasma-surface interactions to the growth mechanism. The nucleation process is followed in situ by spectroscopic ellipsometry assisted by Optical Emission Spectroscopy for the identification of plasma active species and desorbed by-products.

This presentation will describe how the nucleation time on different substrates can be successfully tuned, either delayed or accelerated, thanks to appropriate in situ surface treatment parameters, without inducing any significant perturbation in the subsequent steady state layer growth. These results will be discussed in view of literature data and potential applications to the development of selective ALD.

9:00am **TF+AM+EM+PS-TuM4 Topographical Selectivity with BN Electron-Enhanced ALD***, **Jaclyn Sprenger**, A.S. Cavanagh, H. Sun,* University of Colorado at Boulder*; A. Roshko, P. Blanchard,* National Institute of Standards and Technology*; S.M. George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) is a new growth technique using sequential self-limiting exposures of electrons and precursor. The electrons produce dangling bonds at the surface through the process of electron stimulated desorption (ESD). The dangling bonds then facilitate the adsorption of precursor resulting in film growth. Because the electron flux is directional, EE-ALD can be used for selective area deposition. For portions of the sample that are masked from the e^--beam, no dangling bonds are produced and no film growth occurs. Additionally, any portion of the surface that is parallel to the e^--beam, e.g. the walls of a trench, may be considered topographically masked because the e^--beam is not incident on the surface.

The topographically selective area deposition by EE-ALD was investigated by depositing boron nitride (BN) EE-ALD films on a trench structure. EE-ALD of BN has been demonstrated using sequential exposures of borazine ($B_3N_3H_6$) and electrons (50-450 eV) at room temperature [1]. GaN [2] and Si [3] have also been deposited earlier using EE-ALD. The topographical selectivity was investigated by growing an EE-ALD BN film on a trench structure. On the vertical walls of a trench structure, aligned parallel to the e^--beam, there should be no electron flux and no film. In contrast, the top and bottom of the trench will receive the full flux of the e^--beam. To test these ideas, high resolution TEM images were recorded after 1000 cycles of BN EE-ALD on a trench structure.

BN films were observed on the top and bottom of the trench. For the trenches used in this study, the side walls were not vertical. Some BN film deposition did occur on these sidewalls, but at a lower growth rate than the horizontal surfaces at the top and bottom of the trench. The electron flux on the side walls was reduced by a factor of cos θ where θ is the angle between the surface normal of trench wall and the e^--beam. Incorporating the reduced electron flux into the model for EE-ALD film growth showed excellent agreement with film thicknesses observed on the trench walls. The topographic selectivity of EE-ALD, demonstrated with BN, coupled with a metal chemistry, would offer a promising solution to challenges such as the bottom-up-fill of conductors in trenches or vias.

[1] J. K. Sprenger, H. Sun, A. S. Cavanagh, A. Roshko, P. T. Blanchard and S. M. George, J. Phys. Chem. C. DOI: 10.1021/acs.jpcc.8b00796 (2018).

[2] J.K. Sprenger, A.S. Cavanagh, H. Sun, K.J. Wahl, A. Roshko and S.M. George, Chem. Mater. 28, 5282 (2016).

[3] J.K. Sprenger, A.S. Cavanagh, H. Sun, and S.M. George, J. Vac. Sci. Technol. A. 36, 01A118 (2018).

9:20am **TF+AM+EM+PS-TuM5 Optimization by In situ Ellipsometry of ALD and ALE Successive Steps for the Selective Atomic Layer Deposition of Ta_2O_5 on TiN and Si.***, **Vincent Pesce**, C. Vallée,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; R. Gassilloud,* Cea Leti, France*; A. Chaker, M. Bonvalot, B. Pelissier,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; N. Nicolas,* Cea, France*; A. Bsiesy,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

The drastic reduction of microelectronic device dimensions, traditionally achieved through a photolithography process, requires more and more stringent process conditions in this top-down approach. Recent developments in atomic layer deposition processes (ALD) have shown that a new bottom-up approach is possible by the combination of ALD and Atomic Layer Etching (ALE) steps for the selective growth on patterned surfaces [1]. Indeed, it has been shown that the nucleation kinetics in the initial stages of a deposition process is strongly dependent on the chemical state of substrate surfaces. Thus, different nucleation delays can be achieved on patterned substrates, leading to significant variation of thickness in spite of a similar growth rate after nucleation (in the steady state). Prior to precursor deposition, a first step is carried out, which activates or inhibits nucleation sites on patterned substrates. For instance, an O_2/CF_4 plasma treatment leads to the formation of a fluorocarbon polymer, whose thickness depends on the chemistry of the surface: its thickness may be less on Si as compared to TiN, because SiF_4 molecules are more volatile than their TiF_4 counterparts. In turn, this CF_x rich layer can serve as a passivation layer to alter the nucleation sites during the subsequent deposition process. Similarly, an oxidation plasma treatment serves to activate nucleation sites through the formation of metal-oxygen

bonds on the patterned substrate, which in turn favors an immediate growth during deposition process.

In this work, we have investigated the impact of both chemical and physical surface interactions during the deposition of Ta_2O_5 in a PE-ALD process. These investigations have been carried out in a FlexAL PEALD tool equipped with an ALE bias system developed by Oxford. A selective deposition super cycle has been defined, which consists in alternating a CF_4 plasma treatment with a Ta_2O_5 ALD deposition cycle with an O_2 plasma as oxidation step. In situ ellipsometry measurements have been used to investigate the impact of ion bombardement and the CF_x layer growth during the optimization of the ALE parameters.

These measurements have been correlated to ex situ XRR and XPS to confirm the thickness on both Si and TiN substrates and analyze the chemistry of the different layers or interfaces.

[1] R. Vallat et al. "Selective deposition of Ta_2O_5 by adding plasma etching super-cycles in plasma enhanced atomic layer deposition steps." *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 35.1 (2017): 01B104. (DOI: 10.1116/1.4965966)

9:40am **TF+AM+EM+PS-TuM6 ALD and PEALD of ZnO on MoS_2 and WSe_2*,* *Timothy N. Walter*[1]*, S. Lee,* The Pennsylvania State Univeristy*; M. Chubarov,* The Pennsylvania State University*; X. Zhang,* The Pennsylvania State Univeristy*; T.H. Choudhury, J.M. Redwing,* The Pennsylvania State University*; T.N. Jackson, S.E. Mohney,* The Pennsylvania State Univeristy**

Inducing nucleation on the inherently passivated surfaces of 2D materials such as transition metal dichalcogenides (TMDs) can be challenging for atomic layer deposition (ALD); however, this situation also presents an opportunity for selective growth by ALD. Additionally, ZnO/TMD heterojunctions have favorable band alignments for catalysis and offer possibilities for nanoscale electronic devices including transparent electronics, photodiodes, and piezo-phototronics. This work explores the growth of ZnO on the TMDs MoS_2 and WSe_2 using thermal ALD, thermal ALD with UV-O_3 surface pre-treatment, and plasma enhanced ALD (PEALD). Depositions were performed on both few-layer exfoliated flakes and coalesced single-layer films (with scattered 2- or 3-layer islands) that were already grown by gas source chemical vapor deposition (CVD). Samples were characterized by atomic force microscopy (AFM), Raman spectroscopy, photoluminescence (PL), and X-ray photoelectron spectroscopy (XPS) before and after deposition of ZnO. For both MoS_2 and WSe_2, thermal ALD of ZnO using diethyl zinc (DEZ) and water at 125 °C resulted in a long nucleation delay on the TMD surfaces, showing selectivity against ZnO growth on TMDs compared to the surrounding SiO_2/Si substrate. Even after hundreds of cycles, very little change was detected by XPS, Raman spectroscopy, or AFM; however, nucleation did occur at defects and caused surface roughness to increase. UV-O_3 pre-treatment before thermal ALD yielded different results on MoS_2 compared to WSe_2. UV-O_3 functionalizes MoS_2 for nucleation and subsequent growth of ZnO without destroying the underlying MoS_2; however, UV-O_3 fully oxidized regions of the WSe_2 surface and promoted nucleation. PEALD using DEZ and N_2O on both TMDs resulted in a conformal and smooth film, but it oxidized the top layer of the TMDs according to XPS. In conclusion, UV-O_3 pre-treatment and plasma-enhanced deposition allow for nucleation and growth of ZnO on TMD substrates, sometimes to the detriment of the top layer of material; however, the planar surfaces of 2D materials resist nucleation for hundreds of cycles of thermal ALD.

11:00am **TF+AM+EM+PS-TuM10 From Fundamental Insights into Growth and Nucleation Mechanisms to Area-selective Deposition*, Annelies Delabie,*** IMEC & KU Leuven, Belgium*; J. Soethoudt,* KU Leuven, Belgium*; G. Pourtois, S. Van Elshocht, K. Barla,* Imec, Belgium*; F. Grillo, E. Marques, J.R. van Ommen,* TU Delft, Netherlands **INVITED**

Area-selective deposition holds the potential to build structures from the bottom up, only where needed, with atomic precision. It is gaining importance for manufacturing of nano-electronic devices as it enables self-aligned deposition for accurate pattern placement and bottom-up deposition in trenches or holes. It can simplify complex integration flows and implies significant cost reduction. The key to area-selective deposition is surface chemistry, as it is based on the surface dependence of deposition techniques like chemical vapor deposition (CVD) and atomic layer deposition (ALD). Today, however, only few industrial processes make use of area-selective deposition, mainly because only few materials can be deposited with sufficient selectivity. In addition, defectivity is a great challenge, as substrate inhibition is often associated with island growth. Detailed insights into the surface chemistry and nucleation mechanisms is essential, as this insight can be used to expand the material combinations accessible by area-selective deposition, as well as to design defect removal strategies. Finally, area-selective deposition is affected by patterning due to changes in surface composition and/or due to diffusion. This illustrates the need for understanding and optimization of the processes in patterns with relevant dimensions. In this work, we review our current understanding of the inherent surface dependence of ALD processes. We show how insight into the growth and nucleation mechanisms of ALD can be applied to enable area-selective deposition with defect removal solutions.

11:40am **TF+AM+EM+PS-TuM12 DETA SAMs as ALD Ru Inhibitor for Area-selective Bottom-up Interconnects*, Ivan Zyulkov,*** IMEC & KU Leuven*; S. Armini,* IMEC, Belgium*; S. De Gendt,* IMEC, KU Leuven, Belgium

Replacement of Cu interconnects by an alternative metal will be required beyond 32 nm metal pitch in order to decrease the metal line resistance and prevent IC failure due to the Cu electromigration. Based on recent studies, Ru has several advantages when compared to Cu, which make it an attractive candidate for the Cu replacement: i) lower thickness dependence of the resistivity due to a short electron mean free path (6.6/4.9 nm for Ru vs 39.9 nm for Cu), ii) higher melting temperature (2334 ºC for Ru vs 1032 ºC for Cu) which represents better Ru resistance to electromighration and iii) possibility of integration without a diffusion barrier, resulting in a larger effective metal area. However, conventional electrochemical and electroless deposition methods used in IC manufacturing are not available for the Ru metallization. Additionally, downscaling of the metal structures down to 10 nm causes metal lines filling issues even using conformal ALD, since seams are likely to be formed due to trench pinch-off. As a solution, area selective deposition (ASD) can be exploited, allowing bottom-up and void-free filling of high aspect ratio structures. In addition, ASD of Ru can find application in advanced patterning schemes.

This work is focused on ASD of Ru in a via area of the interconnect structure. In this case ALD selectivity to metallic via bottom (underlying metal line) should be achieved with respect to organosilicate glass (OSG) via sidewalls. In this work, thermal ALD Ru using an ethylbenzene-ethyleyelohexadiene (EBECHRu) precursor with O_2 co-reactant was used. The precursor molecule has ethyl-cyclohexadienyl ligands, which are expected to show a preferential interaction/ inhibition with specific surface groups. In order to passivate the hydroxy-terminated OSG sidewalls against the Ru deposition different siloxane derived self-assembled monolayers (SAMs) were used. According to RBS and SEM analysis, (3-trimethoxysilylpropyl)diethylenetriamine (DETA) SAMs provide more than 300 cycles inhibition of the ALD Ru growth on Si oxide and OSG. XPS, FTIR and spectroscopic ellipsometry on the SAM film before and after ALD are compared in order to identify relevant selectivity mechanisms. In order to prevent DETA passivation of the Cu interface where ALD Ru is expected to grow for the bottom-up via fill, undecanethiol (UDT) SAMs were used as a selective sacrificial Cu protection before the DETA deposition. The thiol SAMs can be removed from the Cu surface at 250 ºC while silane (DETA) is stable on the dielectric surface at temperatures above 350 ºC and higher. The double SAM and area selective bottom-up ALD Ru tested in 45 nm half-pitch lines will be presented.

Thin Films Division
Room 102A - Session TF+AS-TuM

Special Session in Honor of Paul Holloway: Luminescent Materials Growth, Synthesis and Characterization

Moderators: Sean Jones, National Science Foundation (NSF), Jay Lewis, Defense Advanced Research Projects Agency

8:00am **TF+AS-TuM1 INTRO: Special Session Honoring Professor Paul H. Holloway*, Gary McGuire,*** Adamas Nanotechnologies

In light of Professor Holloway's many contributions to the AVS and Thin Film Division special recognition will be given to him during a session dedicated to highlighting his prominence as an educator, scientist and leader. Professor Holloway has held many positions within the AVS including AVS President in 1987, Fellow 1993, Honorary Member 1997, Albert Nerken Award Winner, 1999. The Paul H. Holloway Young Investigator Award is given each year by the Thin Film Division to a deserving recipient. During his career he made major contributions to surface science and surface analysis. His research covered a diverse range of luminescent materials including thin film and powder phosphors, organic light emitting diodes, quantum dots and nanocrystals.

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

8:20am **TF+AS-TuM2 Harnessing Disorder in Detectors**, ***Jay Lewis***, Defense Advanced Research Projects Agency

Most progress in optoelectronic devices has been built upon increasingly perfect materials, where “perfect” implies reducing impurities, point defect, dislocations, and grain boundaries. However the properties of quantum dot devices, such as those demonstrated by the Holloway group, are largely dominated by the surfaces of the nanocrystals. This paper explores the role of nanostructured devices through the lens of DARPA’s Wafer Scale Infrared Detectors (WIRED) program, which seeks to develop infrared detector technology that is inherently disordered. Disorder is a byproduct of the program objective to process detectors directly onto the silicon wafers that are used to process and read out the signals. The program is exploring polycrystalline materials deposited by chemical bath deposition, quantum dot materials deposited by spin or dip coating, as well as traditional III-V compounds deposited at low temperatures compatible with complementary metal oxide semiconductor (CMOS) circuitry. These results are presented in the context of the broader portfolio of DARPA programs seeking to advance the state of the art in imaging and sensing technology.

8:40am **TF+AS-TuM3 Luminescent Materials for Solid State Lighting and Solar Cell Applications**, ***Hendrik C Swart***, *J.J. Terblans, R.E. Kroon, E. Coetsee, M.M. Duvenhage, E. Hasabeldaim, A. Balakrishna, A. Kumar,* University of the Free State, Republic of South Africa; *P.H. Holloway,* University of Florida **INVITED**

Luminescent compounds and materials have numerous uses. The emission properties, whether of a fast decay rate fluorescent material or a slow decay rate phosphorescent material, are defined by the chemical composition and the physical structure of the luminescent material. The crystal field that is determined by the environment in the host material in combination with the various dopant ions with the correct valence state can be used to obtain emissions from the Ultra violet (UV) to the infra-red (IR) wavelength ranges. Phosphor materials have been successfully used to improve the efficiency of various applications. Nanoparticles both undoped and doped with different rare earth elements were synthesized by several synthesized techniques. The major problem that limits solar cells’ efficiency is their insensitivity to the whole solar spectrum which is the so-called spectral mismatch. Therefore, several mechanisms have been explored based on photoluminescence (PL) to convert the solar cell spectrum where the spectral response of the solar cell is low to regions where the spectral response of the solar cell is high. For single crystalline silicon (Si) photovoltaic (PV) cells with a rather small semiconductor band-gap (Eg: 1.12 eV, corresponding to a wavelength of ~1100 nm), the transmission loss of the sub-band-gap photons can still amount to about 20% of the sun’s energy irradiated onto the Earth’s surface. For PV cells with a larger band-gap, such as amorphous Si (Eg: 1.75 eV) solar cells, which are limited to absorb sunlight with wavelengths below 708 nm, manifest even higher near infrared transmission losses. Downconversion, up-conversion (UC) and downshifting are some of the mechanisms that may be applied to improve the spectral response. Upconversion nanoparticles (UCNPs) have shown some promising possibilities to be considered in this respect, however, low UC efficiency of UCNPs is still the most severe limitation of their applications. In downshifting the strong deep level emission (DLE) and near band edge emission could be tuned to cover a wide spectral range. The strong DLE, covering a wide spectral range of ~375-650 nm, signifies the potential optoelectronics application in the near white LED applications. Degradation of the different phosphors during prolonged electron/photon bombardment also played a vital role in their possible applications. Examples of different phosphor materials with different applications such as Solid State Lighting will be shown.

9:20am **TF+AS-TuM5 Fluorescent Nanodiamond for Applications in Whole Body Imaging**, ***Olga Shenderova***, *M.D. Torelli,* Adamas Nanotechnologies; *A. Rickard,* Duke University; *N.J. Nunn,* Adamas Nanotechnologies; *M. Backer,* SibTech; *G.M. Palmer,* Duke University; *G. McGuire,* Adamas Nanotechnologies **INVITED**

Fluorescent nanodiamonds (FNDs) containing color centers exhibit distinct properties including very high biological compatibility, infinite photostability, absence of photoblinking, long fluorescence lifetime (>10 ns), and ease of biofunctionalization, which makes them an attractive alternative to quantum dots, organic dyes, and polymer beads as imaging reagents. Potential applications include background-free and long-term cell imaging, flow cytometry, super-resolution imaging, correlative microscopy, labeling of low-abundance cellular components, fiducial markers, and image guided surgery. In this talk, after reviewing unique properties of FND, their utility for in vivo tumor imaging will be presented. To target receptors overexpressed in cancerous tissue, FNDs were functionalized with vascular endothelial growth factor (VEGF) via click chemistry and then validated *in vitro* for functional activity. Thereafter, FND-VEGF was administered via tail vein injection to nude mice induced with a mammary carcinoma, and mice were analyzed both in vivo and ex vivo via whole body imaging and fluorescence microscopy. Ex vivo micro-spectroscopy utilized the unique spectral signature of nitrogen-vacancy induced fluorescence to demonstrate unambiguous determination of ND translocation to tumorous tissue. The results are placed in the context of FND for whole-body imaging and related applications.

11:00am **TF+AS-TuM10 The Apple does not Fall Far from the Tree: A Serendipitous Journey from Luminescent Materials to Nanoscale Focused Electron (and Ion) Beam Induced Processing**, ***Philip D. Rack***, University of Tennessee Knoxville **INVITED**

I graduated from Paul Hollloway’s group at the University of Florida in 1997 where I studied luminescent materials for electroluminescent displays. If the saying is true that “imitation is the sincerest form of flattery,” then my career speaks volumes of my admiration for the man I had the privilege to call my Phd advisor. In this talk, I will briefly overview some of the luminescent materials research that my group has performed over the years. In true Holloway fashion, I will overview my groups serendipitous journey from luminescent materials to focused nanoscale electron beam induced processing. The remainder of the talk will review topics near and dear to Dr. Holloway’s heart, electron(ion)-gas-solid interactions, and illustrate that appropriate understanding of these interactions can result in the directed growth/etching at the nanoscale. I will overview our groups Monte Carlo simulation to illustrate some of the critical electron(ion)-gas-solid interactions that can rate and resolution limit the deposition and etching processes. Next, I will show how a synchronized pulsed laser can photothermally assist both the etching and deposition processes. Finally, I will review our recent research direction in this area, which is controlled 3d nanoscale printing. Along the way, I will recall anecdotes that illustrate principles learned from the “Holloway way” and hopefully illustrate that I am an apple that did not fall far from the Holloway tree.

11:40am **TF+AS-TuM12 Atomic Layer Deposition of Optoelectronic Materials**, ***Markku Leskela***, *M.K. Ritala,* University of Helsinki, Finland **INVITED**

In optoelectronics, i.e. in electronic devices and systems that emit, detect and control light, the active materials are usually II-VI or III-V semiconductors. Historically in Atomic Layer Deposition (ALD) or Atomic Layer Epitaxy (ALE) as it was called in 70s and 80s, zinc sulfide has been very important material. The ALE technology was developed for manufacturing AC driven thin film electroluminescent displays [1]. Monochromic yellow-black displays based on ZnS:Mn luminescent layer sandwiched between dielectrics and electrodes has been manufactured industrially by ALD continuously since 1984. Besides the luminescent layer, the high-quality oxide layers made by ALE have had an important role as dielectrics and passivation layers in the success of the ACTFEL displays. Multicolor displays can be realized by filtering the broad emission band of ZnS:Mn or using other luminescent material, e.g. green-emitting ZnS:Tb. Despite of intense studies in 1980s and 1990s full-color ACTFEL devices could not been developed to the mass production level because of the missing efficient deep blue-emitting phosphor. Today the strongest developing application area in thin film EL displays is transparent displays used widely in different vehicles [2]. This motivates to re-examine the color displays.

Deposition of epitaxial films of III-V materials is possible with ALD as demonstrated already in 1985 [3]. Processes have been developed for all III-V materials using alkyl compounds for group III metals and hydrides for group V elements as precursors. The advantages of ALD processing compared to MOCVD or MBE have remained, however, modest because of the carbon contamination.

Transition metal dichalcogenides are emerging 2D materials that are potential channel materials in field-effect transistors as well as phototransistors and other optoelectronic devices. The bottle-neck in the large use of these two-dimensional materials is the lack of scalable, low-temperature process for high-quality, large-area films. ALD has been studied as a solution for these problems [4].

In other optoelectronic devices the ALD films find most often use in passivation and encapsulation. Silicon based solar cells is a good example of the former [5] and OLED displays from the latter application area [6].

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Thin Films Division
Room 101A - Session TF-TuM
Emerging Applications for ALD

Moderators: Arrelaine Dameron, Forge Nano, Qing Peng, University of Alabama

8:00am **TF-TuM1 Atomic Layer Deposition of the Metal Pyrites FeS_2, CoS_2, and NiS_2*,* ***Xinwei Wang,*** Shenzhen Graduate School, Peking University, China

The pyrite-type transition-metal disulfides (MS_2, M = Fe, Co, Ni) form a series of compounds that are highly interesting in many aspects. These compounds share the same cubic pyrite crystal structure but differ in the progressive increase of an anti-bonding *d* electron in the conduction band, and as a result, the metal pyrites exhibit very diverse and intriguing electrical magnetic properties from diamagnetic semiconductive to itinerant-electron ferromagnetic and to antiferromagnetic semiconductive. This diversity of the material properties has not only offered a model system platform for fundamental science studies but also enabled tremendous engineering possibilities for practical applications, such as solar cells, lithium/sodium-ion batteries, and electrocatalytic hydrogen evolution, oxygen evolution, and oxygen reduction.

In this presentation, we will show our latest progress on the development of atomic layer deposition processes for the metal pyrites of FeS_2, CoS_2, and NiS_2 (*Angew. Chem.Int. Ed.* 2018, doi:10.1002/anie.201803092). We use the metal amidinate compounds as the precursors for the metals and H_2S plasma as the sulfur source, and we will show that the deposition processes for FeS_2, CoS_2, and NiS_2 all follow ideal layer-by-layer ALD growth behavior over a wide temperature range to produce fairly pure, smooth, pyrite-structure metal disulfide films. We will further show that the ALD FeS_2, CoS_2, and NiS_2 films can be conformally deposited into deep narrow trenches with aspect ratios as high as 10:1, which thereby highlights the broad and promising applicability of these ALD processes for conformal film coatings on complex high-aspect-ratio 3D architectures in general.

8:20am **TF-TuM2 Atomic Layer Deposition of Yttrium Fluoride and Yttrium Oxyfluoride Films with Tunable Stoichiometry***,* ***Jasmine Wallas***[1]*, J.A. Murdzek, D.K. Lancaster, A.S. Cavanagh, S.M. George,* University of Colorado at Boulder

YF_3 and YO_xF_y are materials with excellent chemical and thermal stability. YF_3 and YO_xF_y have both demonstrated exceptional corrosion resistance to highly reactive plasmas. In this work, YF_3 atomic layer deposition (ALD) was developed using tris(butylcyclopentadienyl) yttrium and HF-pyridine as the reactants. The ALD of YO_xF_y alloys was also demonstrated with tunable control of the oxygen and fluorine stoichiometry. This tunable control was difficult because of the rapid exchange of oxygen by fluorine in Y_2O_3 and YO_xF_y alloys during HF exposures.

In situ quartz crystal microbalance (QCM) analysis of YF_3 ALD revealed linear mass changes and self-limiting behavior using tris(butylcyclopentadienyl) yttrium and HF-pyridine as the reactants. The mass gain per cycle (MGPC) was 21.5 ng cm^{-2} at 225°C. The growth rate of YF_3 ALD was also determined to be 0.3 Å per cycle by ex situ X-ray reflectivity analysis. Energy dispersive spectroscopy (EDS) of a cross-section of the YF_3 film yielded a uniform 3:1 ratio of F:Y with low impurities.

YO_xF_y alloys were deposited using H_2O together with the tris(butylcyclopentadienyl) yttrium and HF-pyridine reactants. However, control of the composition of the YO_xF_y alloys was complicated by the facile exchange of oxygen by fluorine during the HF exposures. The oxygen/fluorine exchange was most obvious during HF exposures on Y_2O_3 ALD films when a large mass gain was observed during fluorination. The Y_2O_3 fluorination reaction is believed to be: $Y_2O_3 + 6\ HF \rightarrow 2\ YF_3 + 3\ H_2O$. In addition to the large mass gain, the presence of fluorine throughout the entire film was revealed by X-ray photoelectron spectroscopy (XPS) measurements with depth-profiling. The XPS depth-profiling results are consistent with rapid fluorine diffusion in the Y_2O_3 and YO_xF_y films.

Various super-cycles were employed to obtain YO_xF_y alloys with particular F:O ratios. The most reliable method for composition control was defined by performing HF exposures between intervals of Y_2O_3 ALD. The number of Y_2O_3 ALD cycles and the length of the HF exposure could be varied to produce YO_xF_y alloy films with tunable and consistent composition as measured with XPS depth-profiling. The growth rate of the YO_xF_y alloy films was dependent on the number of Y_2O_3 ALD cycles before the HF exposures. The super-cycles with a larger number of Y_2O_3 ALD cycles before the HF exposures produced higher growth rates resulting from the higher growth rate of 0.8 Å per cycle for Y_2O_3 ALD.

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8:40am **TF-TuM3 Synthesis of Single Phase Two-dimensional SnS_2 by Plasma-enhanced Atomic Layer Deposition***, J.J. Pyeon, I.-H. Baek,* Korea Institute of Science and Technology*; T.-M. Chung,* Korea Research Institute of Chemical Technology*; J.H. Han,* Seoul National University of Science and Technology*; C.-Y. Kang,* ***SeongKeun Kim,*** Korea Institute of Science and Technology, Republic of Korea

Two-dimensional (2-D) metal chalcogenides have received great attention because of their unique characteristics. A challenge in implementing 2-D metal chalcogenides in emerging devices is to synthesize a well-crystallized layer over large areas at temperatures compatible with current fabrication processes. Tin disulfide, a n-type layered semiconductor, is a promising candidate for realizing large-area growth at low temperatures because of its low melting point. However, tin sulfides exist in various phases such as SnS, Sn_2S_3, and SnS_2. It is challenging to form a single phase SnS_2 at low temperatures.

Here, we demonstrated the synthesis of high-quality SnS_2 by plasma-enhanced atomic layer deposition (PEALD). All the processes were performed below 300 °C, which is compatible with current electronic devices. Stoichiometric SnS_2 films were formed. It was verified from various techniques such as Raman spectroscopy, x-ray photoelectron spectroscopy, and x-ray diffraction that a single phase of SnS_2 was formed. It was found that the microstructure of the SnS_2 films was strongly dependent on the growth temperature. Vertically aligned SnS_2 flakes were observed in the SnS2 grown at relatively high temperatures (210 - 270 °C). Through a two-step process – a seed layer growth at low temperature (150 °C) and a main layer growth at high temperatures (240 – 270 °C), well crystallized SnS_2 layers were aligned in parallel to the substrate. Moreover, the properties of field-effect transistor using the SnS_2 films were investigated. A high on/off ratio of ~ 10^6 and a moderate field-effect mobility of ~ 1 cm^2/Vs were achieved from the devices utilizing SnS_2 grown by PEALD.

9:00am **TF-TuM4 Phase Selective, Low Temperature Growth of TiO2 by Atomic Layer Epitaxy***,* ***Jason Avila,*** *D.R. Boris, S.B. Qadri, J.A. Freitas, S.G. Walton,* U.S. Naval Research Laboratory*; C.R. Eddy, Jr.,* U. S. Naval Research Laboratory*; V.D. Wheeler,* U.S. Naval Research Laboratory

Atomic layer deposition (ALD) of TiO_2 has been widely explored recently due to its promise in non-volatile resistive switch, high-k gate dielectric, solar cell, and photocatalytic applications. This growth method has become increasingly useful as device dimensions are reduced and non-planar complexity is increased. To facilitate epitaxial films at low growth temperatures (T_g), many have investigated plasma, laser or photon, or electron enhanced ALD processes. Specifically for TiO_2, it would be beneficial to selectively grow epitaxial anatase or rutile phases in order to tailor optical, catalytic and electrical properties for the required application. Typically, TiO_2 phase selectively is attained by varying the underlying substrate, Ti and/or oxidation precursor, or T_g. However, here we demonstrate phase selectivity of high quality epitaxial TiO_2 films simply by adjusting plasma gas composition, pressure and Tg.

A Veeco Fiji G2 reactor was used to deposit TiO_2 films on different sapphire orientations (c-, m-, a-) with tetrakis(dimethylamido)titanium (TDMAT) and either Ar/O_2 or pure O_2 plasma at 100-350° C. Previous reports indicate that tuning the ion energy, specifically through substrate biasing, can influence TiO_2 film crystallinity and phase [1]. The high pumping speed and large gas flow range available in this specific ALD system provides a wide variation in operating pressures (7-100's mTorr), which effectively allows tuning of plasma characteristics. Operating at relatively low pressures (9-21mTorr) resulted in a significant flux (0.5-1.5x10^{19} $m^{-2}s^{-1}$) of energetic ions (30-50eV), with both the flux and energy decreasing as the pressure is increased. The low pressure conditions yield high-quality epitaxial films at

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

all temperatures, which differs from previous reports using these specific precursors [2,3] likely due to these unique plasma conditions.

Gas composition during the plasma step also had a substantial effect on growth rate, TiO_2 phase, and strain. At T_g < 300° C, the growth rate was increased from 0.5 to 0.7 Å /cycle by switching from Ar/O_2 to pure O_2. Moreover, an O_2 plasma produced only rutile TiO_2 films, with less strain, independent of growth temperature or underlying substrate orientation. In contrast, films deposited with an Ar/O_2 plasma show a phase dependence on temperature and substrate. Films on c-plane Al_2O_3 go from anatase at T_g below 200° C to rutile above 300° C. The films on m-plane Al_2O_3 are rutile independent of temperature.

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9:20am **TF-TuM5 Substrate Biasing During Plasma Atomic Layer Deposition: From Stress-controlled Oxides to Low-resistivity Nitrides***,* ***Harm Knoops,*** Oxford Instruments, The Netherlands*; T.F. Faraz, K. Arts, S. Karwal, M.C. Creatore, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Thin films grown by plasma atomic layer deposition (ALD) can be strongly influenced by the energy of the ions present during the plasma step. Here we report on how using enhanced energies influence the material properties of many oxides and nitrides.[1,2] To utilize these effects, discussion on promising process schemes and which material properties are key is needed. This work will discuss application relevant aspects and focus on the stress-control of oxides and the reduction of resistivity for nitrides.

Ion energy control during plasma exposure was carried out in a commercial 200-mm remote plasma ALD system (Oxford Instruments FlexAL) equipped with RF substrate biasing. Substrate biasing increased the refractive index of TiO_2 at 300 °C to 2.54±0.03, mass density to 4.2±0.2 g/cm^3, and the crystal phase went from anatase to rutile. ALD of TiO_2 at 150 °C typically yields amorphous films, but using a bias crystalline rutile phase was obtained. Besides these modified material properties the residual stress was altered from tensile (176±50 MPa) to strongly compressive (-2430±50 MPa) and by choosing the bias voltage and duration, a close to zero stress could be achieved (−25±50 MPa). Stress control of oxides on planar surfaces can be beneficial for several devices through: anti-reflective TiO_2 coatings, stressed Al_2O_3/HfO_2 gate oxides, and compressive Ta_2O_5 barrier layers.

For transition metal nitrides, enhancing ion energies was observed to have pronounced effects on chemical composition and microstructure.[1,2] Energetic ion bombardment lowered film resistivity down to 139±10 μΩcm at -187V bias for TiN and increased the crystallinity. The ability to deposit crystalline films on temperature sensitive substrates (e.g., conductive TiN on polymer substrates) could be a benefit for low temperature electronics. Oxygen impurity content was observed to be significantly reduced by substrate biasing. Oxygen contents of 3±2 at. % for TiN and <2 at. % for HfN_x were achieved without taking special care of low oxygen backgrounds. Ar/H_2 plasma with biasing was found to allow removal of surface oxygen, while simply extending the plasma exposure without applying bias did not lead to such removal. The reduction of oxygen content by these plasmas also suggests a possible use in applications as a chemical sputter clean of surfaces. In general the application of biasing brings the processing of plasma ALD closer to the realm of ALE and atomic scale processing. Possible related processing schemes and the general trends for nitrides and oxides will be discussed.

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9:40am **TF-TuM6 Development of Novel Superconducting ALD Films for Astronomy Applications***,* ***Frank Greer,*** *P. Day, B. Eom, H. Leduc,* Jet Propulsion Laboratory, California Institute of Technology

Future sub-millimeter telescopes and spectrometers have the potential to revolutionize our understanding of the formation of the modern universe. Sub-millimeter astronomy can probe the fine structure of the cosmic microwave background, giving glimpses into the early universe immediately following the Big Bang. Recent advances in design have enabled the production of large arrays of cryogenically cooled superconducting detectors with sufficient sensitivity for photon counting applications. Transition edge sensors (TES) and other types of detectors, fabricated from thin films of metal nitrides such TiN, NbN, TaN, VN, and their mixtures, are cryogenically cooled to just below their superconducting transition temperature. Photons in the X-ray or sub-millimeter wavelength range can be detected because their absorption will cause the temperature of an appropriately designed TES array element to rise just enough to cause it to have a finite resistance. However, while conventional deposition processes such as physical sputtering have been sufficient for small area arrays and proof of concept sensors, critical parameters such as the superconducting transition temperature are strongly sensitive to film thickness, stochiometry, and interface quality. Therefore, as the size of an individual detector array or the number of detector arrays on a wafer increases, it becomes more and more difficult to fabricate them with sufficiently uniform response in sufficient quantity to populate the focal plane of a large telescope. We are utilizing the uniformity and compositional control provided by atomic layer deposition to overcome these limitations for the fabrication of transition edge sensors as well as other applications requiring superconducting thin films.

11:00am **TF-TuM10 Atomic Layer Deposition of Cobalt Nanoparticles***,* ***Gerben van Straaten,*** *W.M.M. Kessels, M.C. Creatore,* Eindhoven University of Technology, The Netherlands

Cobalt nanoparticles (NPs) with well-defined sizes are highly sought after for a variety of catalytic processes. For example, cobalt NP catalysts for the Fischer-Tropsch process, used in industry to upgrade coal and natural gas into fuels, show a sharp maximum in activity for a particle diameter of ca. 8 nm[1]. Such size-sensitive catalytic processes require conformal deposition of cobalt NPs throughout porous substrates, requirements that can potentially be met by ALD.

ALD of catalytic platinum-group metal NPs with narrow size distributions has been exhaustively studied. However, compared to these systems, ALD of cobalt metal NPs is much more challenging due to their high reactivity. To our knowledge, Co NPs have only been obtained by reduction of ALD-deposited Co_3O_4 NPs [2] or by reduction and subsequent melting of ALD-deposited Co_3O_4 layers [3].

In this contribution, we demonstrate for the first time the direct deposition of Co NPs using Plasma-Enhanced ALD (PEALD)[4]. Cobaltocene ($Co(C_5H_5)_2$) is evaporated at 80°C and dosed for 6s onto an SiO_2 surface held at 250°C. Then, exposure to a remote, inductively coupled plasma fed with NH_3 (1*10^{-2} mbar, 100W) takes place for 10s. After each step, 4s of purging takes place, and saturation of all steps was verified with in-situ Spectroscopic Ellipsometry (SE). By means of TEM we find that Co NPs synthesized via this process consist of a metallic core and an oxide shell formed by air exposure, and that their growth takes places in 3 stages. In the initial stage, up to 150 cycles, a homogeneous coverage of small NPs occurs, with an average diameter of less than 1 nm. Then, after 150 cycles, a second population of larger NPs starts to develop, which increase rapidly in size while retaining a narrow size distribution. After ca. 250 cycles this secondary population is fully developed, with a mean diameter of 7.5 nm and a width of 1.7 nm, but the initial population of small NPs remains, yielding a bimodal size distribution. Growth of this secondary population continues up to ca. 550 cycles, at which point we find from in-situ SE that the NPs coalesce into a continuous film. Preliminary GIXRD and XPS analysis reveals that this film consists of crystalline β-Co but that up to 10 at% of C and N can be present in the film.

Experiments are ongoing to test the catalytic activity of Co NPs synthesized via this method towards the Fischer-Tropsch reaction.

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11:20am **TF-TuM11 Atomic Layer Deposition of Ni-Al-O Catalysts for Water Oxidation***,* ***Jon Baker,*** *J.R. Schneider, J.A. Singh, A.J. Mackus, S.F. Bent,* Stanford University

Electrical energy storage has emerged as an important challenge for societies moving away from fossil fuels toward more renewable sources (e.g. solar and wind) that are intermittent in nature. To rely only on solar and wind for electricity, large scale energy storage systems are required. Among several potential solutions, one promising strategy is to store excess electrical energy in the form of chemical bonds, through electrochemical production of fuels. In particular, electrochemical water

splitting enables the production of hydrogen gas as a chemical fuel from excess electrical energy. However, a major drawback of this strategy is the low efficiency of the oxygen evolution reaction (OER).

To improve the efficiency of the OER, understanding why certain catalysts perform well is a powerful tool in designing new catalysts with better properties. Atomic layer deposition (ALD) has emerged as a strong platform to study catalysts due to its ability to deposit films that are compositionally well-defined. For electrochemical systems, ALD has the added benefit of high uniformity, conformality and precise thickness control; these attributes can minimize potential confounding effects like resistive and mass transport losses, which may affect measurement of a catalyst's intrinsic activity. In this work, we study the effect of aluminum on Ni-Fe-OOH catalysts. While Ni-Fe-OOH catalysts have been reported to have high activity for the OER (nearly independent of synthesis method), the impact of aluminum on this catalyst is not yet well understood, with a wide range of OER activities reported. By using ALD, ternary films of Ni-Al-O were deposited. Introduction of iron was achieved through electrolyte iron-doping, enabling the formation of the quaternary Ni-Al-Fe-OOH catalyst. Electrochemical characterization of sufficiently thin films found that aluminum improved the turnover frequency of Ni-Fe-OOH catalysts by a factor of 3-4. By carefully controlling composition of the catalyst, the effects of aluminum and iron were independently studied. In iron-free catalysts, aluminum was found to improve OER activity; however, its improvement in activity was small compared to the effect of iron. In addition, thickness dependent studies were performed to understand how morphology and synthesis method may impact observed activity. For Ni-Al-Fe-OOH catalysts, a strong thickness dependence in the OER activity was observed. Characterization of the catalysts *ex situ* and under OER operating conditions reveal the likely cause of this thickness dependence is the observed changing morphology of the film with increasing thicknesses.

11:40am **TF-TuM12 Atomic Layer Deposition of Bismuth Vanadate Photoanodes***, **Sudarat Lee**, A.R. Bielinski, S.L. Esarey, J.J. Brancho,* University of Michigan, Ann Arbor*; B.M. Bartlett,* University of Michigan, Ann Arbor*; N.P. Dasgupta,* University of Michigan, Ann Arbor

Bismuth vanadate (BVO) has been widely studied as one of the most promising photoanode materials for photoelectrochemical (PEC) water splitting, owing to a bandgap of 2.4 eV and favorable band positions for water oxidation. However, while BVO has the potential for high anodic photocurrents, it is often limited by electron-hole separation, charge transport, and water oxidation kinetics, requiring development of nanostructured electrode architectures to optimize performance.

Here we demonstrate a new method for fabricating tunable BVO photoanodes deposited by atomic layer deposition (ALD). We present the first deposition of ALD BVO using $Bi(OCMe_2iPr)_3$ as the bismuth source, vanadium(V)oxytriisopropoxide as the vanadium source, and water as the oxidant. The choice of this recently developed Bi precursor provides full control of Bi:V stoichiometry in contrast to the use of earlier Bi precursors such as triphenylbismuth[1], while also providing a per cycle growth rate that is more than three times higher than previous reports.

The BVO films were deposited as a nanolaminate of binary bismuth and vanadium oxides. The films were post-annealed to achieve the photoactive monoclinic $BiVO_4$ phase. Film composition and photocurrent were investigated as a function of deposition pulse ratio and film thickness. The photoactivity of planar ALD BVO was measured in a three-electrode cell under simulated AM1.5G illumination. Sulfite oxidation was used to optimize the BVO deposition conditions independent of co-catalyst performance.We achieved the highest reported photocurrent to date for ALD photoanodes. Using a planar electrode with a 40nm thick BVO film, a photocurrent of >2.6 mA cm^{-2} at 1.23 V_{RHE} was demonstrated for sulfite oxidation and a photocurrent of >1.1 mA cm^{-2} at 1.23 V_{RHE} was demonstrated for water oxidation using an un-optimized cobalt co-catalyst.

ALD provides conformal coverage of high aspect ratio structures. The development of an ALD process for BVO enables core-shell architectures that help address the charge transport and carrier separation challenges by decoupling carrier diffusion and light absorption lengths. To demonstrate this benefit, BVO was deposited on mesoporous tin oxide (ITO) substrates to form 3-D electrode architectures with tunable absorption and charge extraction properties. The photoresponse was enhanced for both sulfite and water oxidation under illumination, demonstrating the power of ALD to improve light absorption and charge extraction in 3-D nanostructured electrode architectures.

*(1)*Stefik, M. Atomic Layer Deposition of Bismuth Vanadates for Solar Energy Materials. *ChemSusChem* **2016,** *9* (13), 1727- 1735.

12:00pm **TF-TuM13 ALD of Cobalt Phosphate Electro-catalyst for Oxygen Evolution Reaction***, **Valerio Di Palma**,* Eindhoven University of Technology, The Netherlands*; G. Zafeiropoulos, M.N. Tsampas,* DIFFER*; W.M.M. Kessels, M.C. Creatore,* Eindhoven University of Technology, The Netherlands

Sunlight-driven water splitting is widely investigated through studies addressing both the development of earth-abundant element-based (photo)electrodes, as well as engineering of compact, efficient and inexpensive devices. One important reason that keeps these systems from being of practical use to date is the sluggish kinetics (high overpotential) of the oxygen evolution reaction (OER). OER is a four electron-proton coupled reaction, while hydrogen evolution reaction (HER) is only a two electron-transfer reaction, and hence usually OER requires a higher overpotential [1].

Electro-deposited cobalt phosphate (CoPi) has been reported as a valid OER catalyst (as bare electrode or as cocatalyst in photoelectrodes) and alternative to rare element compounds [2]. In parallel, ALD is rapidly reaching out also to (photo-)electrocatalytic applications [3,4] and in the present contribution we investigate CoPi growth by ALD and its application as OER catalyst. Compared to electrodeposition, ALD offers the major advantage of tuning the electro-catalyst chemical composition, as we demonstrate in this work.

The CoPi process has been developed using an ABCD scheme, where A, B, C and D are the cobaltocene (CoCp), first oxygen plasma (5 s), trimethylphosphate (TMP) and second oxygen plasma (2 s) dosing steps, respectively. The deposition performed at 300°C results in a growth per cycle of about 1.1 Å, determined by in-situ spectroscopic ellipsometry. Elemental characterization by XPS of the ALD prepared CoPi shows a stoichiometry of $Co_3(PO_{4.3})_2$. The film deposited on FTO/glass is active for OER, as confirmed by cyclic voltammetry. The current density peak measured is about 1.0 mA/cm^2 at 1.4 V vs. NHE (Normal Hydrogen Electrode), comparable to the values reported in literature for electrodeposited CoPi. Furthermore, we investigated the effect of Co-to-P concentration ratio on the OER catalytic activity. To this purpose, the process was modified from the aforementioned ABCD approach into an $(AB)_x(CD)_y$ supercycle approach. The sample prepared with a ratio x-to-y of 12-to-11 showed already a higher current density peak (about 1.2 mA/cm^2 at 1.4 V vs NHE) than the sample deposited without the use of supercycles. This finding highlights the role of Co-to-P concentration ratio on the activity of the catalyst and how the ALD supercycle approach can be adopted to this purpose.

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Thin Films Division
Room 104B - Session TF+PS-TuA

Atomic Layer Processing: Chemistry & Surface Reactions for Atomic Layer Processing

Moderators: Jessica Kachian, Intel Corporation, Keren Kanarik, Lam Research Corporation

2:20pm **TF+PS-TuA1 N-heterocyclic Carbenes on Au and Cu Surfaces*, Cathleen Crudden,*** Queen's University, Canada **INVITED**

N-Heterocyclic carbenes (NHCs) are an exciting new class of ligand for metal surfaces, with potentially interesting applications in patterning and surface functionalization. In this talk, we will address the use of NHCs as ligands for various metal surfaces including coinage and other metals. The functionalization of flat and structured surfaces will be presented and potential applications in etching.

3:00pm **TF+PS-TuA3 Enhancing Nucleation in Platinum Atomic Layer Deposition by Surface Pre-Treatment with Small Organometallic Molecules*, Camila de Paula,*** *L. Zeng, S.F. Bent,* Stanford University

Pt thin films have a wide variety of applications in microelectronics, catalysis, and energy technologies. Since most of these applications require a conformal and pinhole-free thin film, achieving good nucleation is an important requirement. It is believed that a low abundance of dissociated oxygen atoms in the initial stages of the Pt ALD process leads to a nucleation delay and island growth. The nucleation and growth mechanisms have a big impact on the properties of the resulting thin film. If nucleation is inhibited, isolated particles rather than a continuous film may be deposited at low cycle numbers (island-growth), whereas if nucleation is facile, a continuous film may be formed at much lower thicknesses.

While there have been studies focused on the surface reactions that occur during Pt ALD, there is still a lack of understanding of how the substrate surface properties affect nucleation in the initial stages of ALD. There have been reports of methods aimed at enhancing nucleation for specific substrates, such as using a wet piranha etch on silicon substrates. Other studies have used high surface energy adhesion layers, such as W, in order to overcome the nucleation delay.

The goal of this study is to develop a surface pre-treatment technique that enhances Pt ALD nucleation independent of substrate choice, while inducing minimum surface modification of the substrate. In this work, the influence of a sub-monolayer surface coverage of small organometallic molecules on the nucleation and growth of Pt by ALD was studied. It was observed that introducing a short pulse of dimethylaluminum chloride (DMACl) prior to Pt deposition leads to the formation of a continuous film after fewer than 100 cycles on thermally grown silicon oxide vs. over 200 cycles on a non-treated sample. Scanning electron microscopy (SEM), synchrotron based grazing incidence small angle X-ray scattering (GISAXS) and X-ray photoelectron spectroscopy (XPS) were used to analyze the ALD growth mechanism on various treated and untreated substrates. The formation of densely-packed large Pt nanoparticles was observed on the treated surface. GISAXS analysis of the Yoneda-Peak position and pattern showed that the surface treatment leads to nanoparticle coalescence in the very early stages of ALD. Interestingly, a comparison of DMACl to other small organometallic molecules showed that some molecules induced the opposite behavior, instead leading to inhibited Pt ALD. The detailed growth mechanism and possible reaction pathways leading to these results will be discussed.

3:20pm **TF+PS-TuA4 Mass Spectrometer Studies of Volatile Etch Products Produced by Ligand-Exchange Reactions During Thermal Atomic Layer Etching*, Joel Clancey,*** *A.S. Cavanagh, S.M. George,* University of Colorado Boulder

Atomic layer etching (ALE) using sequential, self-limiting surface reactions is an important technique for removing material with atomic layer control. In addition, selective ALE is required for the maskless fabrication of advanced devices as feature sizes become smaller than available lithography. This study reports the study of volatile etch products produced by ligand-exchange reactions during thermal ALE and develops our understanding of selective thermal ALE.

Previous studies have revealed selective thermal ALE in the etching of Al_2O_3, ZrO_2 and HfO_2 using fluorination and ligand-exchange reactions [1]. In this work, we used metal fluoride powders to study volatile etch products produced by fluorination and ligand-exchange reactions during thermal ALE. An *in situ* quadrupole mass spectrometer (QMS) was employed to characterize the etch products produced during the thermal etching of AlF_3, ZrF_4 and HfF_4 powders between 200°C and 300°C using TMA, DMAC, $SiCl_4$ and $TiCl_4$ as the metal precursors.

Thermal Al_2O_3 ALE occurs using HF and TMA as the precursors [2]. For the reaction of TMA with AlF_3 powders, the observed etch products are dimers such as $[AlF(CH_3)_2]_2$ and $[AlF(CH_3)_2\text{-}Al(CH_3)_3]_2$. These products are equivalent to the dimer etch products observed earlier for the reaction of TMA with fluorinated Al_2O_3 during thermal Al_2O_3 ALE. In contrast, Al_2O_3 ALE does not occur with either $SiCl_4$ or $TiCl_4$ as the metal precursors [1]. For the reaction of $SiCl_4$ and $TiCl_4$ with AlF_3 powders, the observed reaction products are $SiFCl_3$ and $TiFCl_3$, respectively. There is halide-exchange between the $SiCl_4$ and $TiCl_4$ metal precursors and the AlF_3 surface. However, there is no observation of volatile Al-containing products that would be consistent with Al_2O_3 etching.

We are developing a matrix that correlates volatile etch or ligand-exchange products with the previous etching results. We are also using density functional theory (DFT) to predict the etch products during thermal ALE. These DFT calculations correctly predict the dimer etch products during Al_2O_3 ALE. This approach is advancing our understanding of selective thermal ALE.

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5:00pm **TF+PS-TuA9 Calculations of Etch Products from Thermal Atomic Layer Etching Using Fluorination and Ligand-Exchange Reactions*, Andrew Cavanagh,*** *J.W. Clancey, S. Sharma, S.M. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of Al_2O_3 can be accomplished using sequential, self-limiting fluorination and ligand-exchange surface reactions with hydrofluoric acid (HF) and trimethyl aluminum (TMA, $Al(CH_3)_3$) as the precursors. Fluorination by HF converts the surface of Al_2O_3 to AlF_3. Ligand-exchange reactions then occur between TMA and the AlF_3 surface. The first ligand-exchange reaction is believed to be: $AlF_3(s) + Al(CH_3)_3(g) \rightarrow AlCH_3F_2(s) + Al(CH_3)_2F(g)$ where "s" indicates a surface species and "g" indicates a gas phase species. Additional ligand-exchange reactions can then react $AlF_2CH_3(s)$ to $AlF(CH_3)_2(g)$. Recent quadrupole mass spectrometry (QMS) studies have observed that the main etch products during Al_2O_3 ALE are the dimers $AlF(CH_3)_2\text{-}AlF(CH_3)_2$ and $AlF(CH_3)_2\text{-}Al(CH_3)_3$. These dimers may be formed from the monomer $AlF(CH_3)_2$ etch product pairing with itself or with the $Al(CH_3)_3$ metal precursor.

To understand these dimer etch products, density functional theory (DFT) calculations were performed on all possible dimers that could be produced from the four possible monomer species ($Al(CH_3)_3$, $Al(CH_3)_2F$, $AlCH_3F$, AlF_3). Each dimer consisted of a pair of bridging ligands between the two Al metal centers and four terminal ligands. The bridging ligands could be (F, F), (F, CH_3) or (CH_3, CH_3). The (F, F) bridges resulted in the most stable dimers while the (CH_3, CH_3) bridges resulted in the least stable dimers. In agreement with the QMS results, these DFT calculations predict that the $AlF(CH_3)_2\text{-}AlF(CH_3)_2$ dimer with a (F,F) bridge and four terminal methyl groups is the most viable etch product.

Additional DFT computational studies have also been performed for ligand-exchange reactions on fluorinated surfaces of Al_2O_3, ZrO_2 and Ga_2O_3 with various metal precursors including $Al(CH_3)_3$, $Al(CH_3)_2Cl$, $SiCl_4$, $GeCl_4$, $SnCl_4$, and $TiCl_4$. These calculations model the ligand-exchange surface reactions during Al_2O_3, ZrO_2 and Ga_2O_3 ALE. For all systems studied to date, the calculations indicate that dimer species are the preferred etch products. Future QMS experiments will observe etch products and compare with the DFT computational studies for a more complete understanding of thermal ALE.

5:20pm **TF+PS-TuA10 Formation of Monolayers and Multilayers During the Vapor-Phase Deposition of Dodecanethiols on Copper Oxide*, David Bergsman,*** *T-L. Liu, R.G. Closser, S.F. Bent,* Stanford University

The deposition of alkanethiols onto copper and copper oxide has been widely studied for use in the passivation of surfaces and as ultrathin blocking layers. The formation of alkanethiol self-assembled monolayers (SAMs) on copper oxide is particularly interesting in that thiols are known

to etch and reduce copper oxide surfaces before ultimately forming a SAM. This has sometimes resulted in films much thicker than expected for a monolayer, leading to the hypothesis that this etching process can create multilayers, though the structure of those multilayers and the mechanism behind their formation were not explored. In recent years, the use of SAMs to enable area-selective atomic layer deposition (ALD) for back-end semiconductor processing has created renewed interest in the study of thiol deposition onto copper, particularly through vapor-phase approaches that can be more easily incorporated into industrial semiconductor fabrication processes. However, no studies have reported the formation of Cu-thiolate multilayers through the vapor-phase.

In this work, we examine the vapor deposition of dodecanethiols (DDTs) onto copper and copper oxide surfaces. We show using atomic force microscopy, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy/electron energy loss spectroscopy that this deposition onto copper oxide surfaces results in the formation of up to 8 nm thick Cu-thiolate multilayer films, rather than SAMs. In contrast, pre-removal of the copper oxide and subsequent DDT exposure creates 2 nm thick SAMs, suggesting that the etching of the copper oxide films by thiol molecules is a key step in the multilayer formation. Synchrotron-based grazing-incidence X-ray diffraction shows these thick films to be highly crystalline, with bilayer thiol structures sandwiched between layers of copper atoms. Crystallites are shown to be oriented both perpendicular and parallel to the surface. We further explore the degradation of these multilayers, demonstrating with scanning electron microscopy and XPS that the films appear to dewet into micron-sized particles after exposure to air. Continued air exposure results in the oxidation of the sulfur and copper in the films on a time scale consistent with DDT monolayers. Finally, the implications of this multilayer formation on area-selective ALD will be discussed.

5:40pm **TF+PS-TuA11 Exchange Reactions During Atomic Layer Deposition: ZnO Conversion to Al_2O_3 by Trimethylaluminum**, ***Tyler Myers**, A.M. Cano, J.W. Clancey, D.K. Lancaster, S.M. George,* University of Colorado at Boulder

Atomic layer deposition (ALD) is typically described by the self-limiting reaction of precursors with surface species that leads to controlled thin film growth. Missing from this picture is the possibility that the precursors can also undergo exchange reactions and convert the surface of the initial substrate to a new material. These exchange reactions are expected if the conversion produces a more thermodynamically favorable reaction product. These exchange reactions may be common during ALD nucleation.

In this study, the exchange between Zn and Al is explored during the initial reaction of trimethylaluminum (TMA) on ZnO films during Al_2O_3 ALD at temperatures from 150-250°C. The exchange is evident from a variety of experimental measurements. Fourier transform infrared (FTIR) investigations detect absorbance changes consistent with ZnO loss and Al_2O_3 gain after the TMA reaction on ZnO ALD films. Quadrupole mass spectrometry (QMS) measurements also observe $Zn(CH_3)_2$ reaction products as expected from the conversion reaction: $3ZnO + 2Al(CH_3)_3 \rightarrow Al_2O_3 + 3Zn(CH_3)_2$. In addition, studies of the effect of TMA exposures on ZnO nanoparticles with a diameter of ~10 nm measured the conversion of ZnO to Al_2O_3. The conversion produces a large mass loss that is consistent with the formation of an Al_2O_3 surface layer. The ZnO to Al_2O_3 conversion is also self-limiting as a function of TMA exposure.

X-ray photoelectron spectroscopy (XPS) and X-ray reflectivity (XRR) investigations are also consistent with the conversion of the surface of ZnO ALD films to Al_2O_3 after the initial TMA exposure. The XPS and XRR measurements both yield an Al_2O_3 surface layer with a thickness of ~1.0 nm on the ZnO ALD film. In addition, quartz crystal microbalance (QCM) measurements detect a substantial conversion of ZnO to Al_2O_3 after the initial TMA exposure during Al_2O_3 ALD. The QCM studies reveal that the mass losses are much more pronounced for thin ZnO films compared with thick ZnO films. In addition, the mass losses are more for ZnO surfaces terminated with $Zn\text{-}CH_3CH_3$ species compared with Zn-OH species.

These studies of the exchange between Zn and Al during the initial reaction of TMA on ZnO illustrate that ALD precursors can convert the surface of the initial substrate to a new material. These exchange reactions must be considered when analyzing ALD nucleation.

6:00pm **TF+PS-TuA12 3D Feature Profile Simulation Coupled with Realistic Plasma Surface Reaction Model for ALE Process**, ***YeongGeun Yook**, H.S. You, J.H. Park,* Chonbuk National University, Republic of Korea*; D.H. You,* KW Tech, Republic of Korea*; K.S. Choi,* Chonbuk National University, Republic of Korea*; W.S. Chang,* National Fusion Research Institute, Republic of Korea

Recently, atomic layer etching (ALE) processes have attracted much interest for sub-10nm semiconductor fabrication process. Notably, a cyclic plasma-enhanced fluorocarbon ALE process using the conventional plasma etch tools has investigated for its selective etching and atomic-level control. In spite of its superior merits, the detailed studies remain to apply sub-10nm 3D nanoscale feature patterns due to its complexity. To address this issue, we developed a 3D feature profile simulator which was composed of a Zero-D bulk plasma simulator, a multiple-level set moving algorithm based on a hash map, a GPU based ballistic transport algorithm, and a surface reaction model. In this work, we focus on the development of a transient surface reaction model of ALE process to capture the realistic surface reaction. Finally, 3D feature profile simulations coupled with the surface reaction model were verified with experimental data. We believe that this approach enables us to understand unveiled phenomena of ALE process.

Thin Films Division
Room 102A - Session TF+SS-TuA
Organic/Inorganic Materials and Interfaces

Moderator: Matthew Richard Linford, Brigham Young University

2:20pm **TF+SS-TuA1 Chemical Interactions at Hybrid Interfaces: An In Situ Investigation of Organic/Inorganic Systems**, ***Sven Pletincx**,* Vrije Universiteit Brussel, Belgium*; L. Trotochaud,* Lawrence Berkeley Lab, University of California, Berkeley*; L.-L. Fockaert, M. Meeusen, J.M.C. Mol,* Technical University Delft, Netherlands*; H. Bluhm,* Lawrence Berkeley Lab, University of California, Berkeley*; H. Terryn, T. Hauffman,* Vrije Universiteit Brussel, Belgium

The durability of hybrid systems is mainly determined by the different phenomena occurring at the organic/inorganic interface. However, analyzing this solid/solid or liquid/solid interface under technologically relevant conditions is challenging. Recently, the *in situ* investigation of these so-called buried interfaces is done by monitoring ultrathin polymer films onto a metal oxide substrate by ambient-pressure photoelectron spectroscopy (APXPS).[1,2] Here, we show that APXPS with a conventional X-ray source can be used to study the effects of water exposure on the interaction of different acrylic coatings with aluminum oxide.

The deposition of this nanometer thin overlayer is often carried out by reactive adsorption from dilute polymer solutions. However, the influence of the solvent on the metal oxide chemistry is seldom taken into account in interface studies. An integrated spectroelectrochemical setup of ATR-FTIR Kretschmann and Odd Random Phase multisine Electrochemical Impedance Spectroscopy (ORP-EIS) allows to monitor the influence of the solvent on the metal oxide surface. An aluminum layer is sputtered on an IR transparent crystal, the IR signal at the interface is amplified because of the Kretschmann effect, and a near-interface spectrum of the organic/oxide surface is obtained. The occurring interface processes can be followed with infrared spectroscopy while simultaneously, the PVD layer acts as a working electrode. This allows to determine the electrochemical properties of the overall hybrid system, studied by ORP-EIS.[3]

After the characterization of the solvent interactions, *in situ* ATR-FTIR Kretschmann/ORP-EIS is used to study the effect of an electrolyte on an acrylic polymer/metal oxide system. This way, we have direct access to the interface, and the influence of an above-the-polymer electrolyte (i.e. H_2O) can be probed. Also the study of covalent bonding, such as the interfacial interactions of silane adhesion promotors are investigated. This work shows that by using ultrathin films and a set of recently developed techniques, it is possible to non-destructively and *in situ* probe interfacial changes in hybrid systems.

1. Pletincx, S. *et al.* In Situ Characterization of the Initial Effect of Water on Molecular Interactions at the Interface of Organic/Inorganic Hybrid Systems. *Sci. Rep.***7,** 45123 (2017).

2. Pletincx, S. *et al.* Unravelling the Chemical Influence of Water on the PMMA/Aluminum Oxide Hybrid Interface In Situ. *Sci. Rep.***7,** 13341 (2017).

3. Hauffman, T. *et al.* Measuring the adsorption of ethanol on aluminium oxides using odd random phase multisine electrochemical impedance spectroscopy. *Electrochem. commun.* **22,** 124–127 (2012).

2:40pm **TF+SS-TuA2 Microscopic and Spectroscopic evidence of Odd-Even Effect in Self-Assembled Monolayers of Biphenyl-Substituted Fatty Acid on Ag(111)**, ***Anna Krzykawska,*** Jagiellonian University, Polska; *P. Cyganik, M. Szwed, J. Ossowski,* Jagiellonian University, Poland

Self-assembled monolayers (SAMs) have been broadly studied as a model system for inorganic-organic interface in molecular electronics and biosensing devices. Current standard in SAMs formation is based on using sulfur as an anchoring group to the metal substrate. In our recent paper[1] we have indicated that by replacing thiol headgroup by carboxylic, a highly interesting alternative is obtained, particularly when 2D ordering, SAM fabrication time and stability in ambient conditions are of great importance. Following this first observation made for a specific system, in the current work we have investigated a homolog series of SAMs based on biphenyl-substituted fatty acids on Ag(111) in the form of $(C_6H_4)_2$-$(CH_2)_n$-COO/Ag (BP*n*COO/Ag, n = 1-4). The series of experiments were carried out using infrared reflection absorption spectroscopy (IRRAS), scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The results of this combined microscopic and spectroscopic analysis demonstrate very strong dependence of the structural properties on the number of the CH_2 groups in the short aliphatic linker. Monolayers with n = even show highly ordered and stable structures. In contrast, SAMs with *n = odd* have disordered liquid-like structure with more canted orientation of the molecular backbone and the carboxylic headgroup, which results in lower packing density and film thickness compared to the even-numbered SAMs. By comparing obtained results with former odd-even effects reported for analogues SAMs based on thiols and selenols[3,4], a common, qualitative model relating the odd-even effect to the monolayer stability and structure will be discussed. Our results demonstrate that for BP*n*COO/Ag, this odd-even effect is particularly strong and fully controls the ability of molecules to form highly ordered structures. This observation seems to be of key importance for the design of SAMs based on the carboxylic group, which, for correctly designed molecules, forms much better 2D-ordered structures compared to commonly used thiols.

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3:00pm **TF+SS-TuA3 CVD of Thin Polymer Films for Engineered Material Properties**, ***AnnaMaria Coclite,*** Graz University of Technology, Austria **INVITED**

Functional thin films offer innovative solutions for many technological applications: organic electronics, smart devices for biotechnology, microfluidics, membrane technology, sensors and drug delivery systems. The development of functional thin films, engineered to achieve all the desired properties, requires advanced growth techniques. The development of dry growth methods - based on vacuum- aims to complement and enlarge the applicability of functional thin films to fields where the presence of solvent is detrimental.

Successful results in terms of rationally designed micro- and nanoengineered materials will be demonstrated using as a case of study the growth of functional polymers by initiated CVD (iCVD). The high versatility of iCVD in driving application-specific properties into the material, creating a platform for the implementation of polymeric coatings into device fabrication will be discussed.

Layered nanostructures in proton conductive iCVD polymers were investigated though X-ray based methods. The polymers crystallize in a bilayer structure, perpendicular to the substrate surface, formed by perfluorinated pendant chains. Acid moieties were introduced to form ionic channels among the bilayers –parallel to the substrate surface- which can be responsible for proton conduction. This one-step polymerization process has the potential to manufacture inexpensive, high quality membranes for proton exchange membrane fuel cells.

Another case of study will be presented in the field of multi-stimuli-responsive materials. In particular, the material of interest in this case is a hydrogel that changes its size and shape when stimulated by light and humidity. Hydrogels are known for their dynamic swelling response to aqueous environments. A chemical functionalization of the hydrogel surface was performed to add other stimuli-responsive functionalities and obtain a smart material that responds to two stimuli. Modifying the hydrogel surface with solution-based methods is often problematic because of the damages caused by the permeation of solvents in the hydrogel. This issue is completely bypassed by the use of solvent-free techniques, like iCVD.

4:20pm **TF+SS-TuA7 Organosilicon Functionally Nanostructured Films as Engineered Interlayers for Hybrid Materials**, ***Vladimir Cech,*** Brno University of Technology, Czech Republic; *J. Houdkova,* Institute of Physics, Academy of Sciences of the Czech Republic; *M. Branecky, T. Plichta,* Brno University of Technology; *J. Zemek,* Institute of Physics, Academy of Sciences of the Czech Republic

Thin films of organosilicones synthetized in low-temperature plasma constitute a class of materials with a rich and varied scientific background. This class of materials in the form of hydrogenated amorphous carbon-silicon (a-CSi:H) films has a distinctive characteristic that distinguishes it from other thin films – the ability to vary and control the degree of organic/inorganic character and crosslinking of carbon-silicon network by appropriate choice of fabrication variables. Oxygen atoms can be incorporated in organosilicon film to form new chemical bonds (Si-O, C-O, C=O) and vary the mechanical properties of hydrogenated amorphous carbon-silicon oxide (a-CSiO:H) films by modifying the carbon-silicon network. However, a multilayer rather than single layer film can fulfill specific functions not only in sophisticated electronic, optical, mechanical, and biomedical devices, but also in hybrid materials (composites and nanocomposites) with controlled interphase.

Functional multilayer nanostructures with controlled distribution of mechanical properties across the nanostructure were constructed from oxygen-free (a-CSi:H) and oxygen-bound (a-CSiO:H) individual layers deposited at different effective power or pulse period from tetravinylsilane and tetravinylsilane in a mixture with oxygen gas, respectively, by plasma-enhanced chemical vapor deposition operated in pulsed mode. XPS depth profiling using argon cluster ion beams was used to determine the atomic concentration of carbon, silicon, and oxygen in individual layers forming the multilayer nanostructures with a total thickness of about 100 nm. The XPS analysis revealed that the oxygen-free layers were oxidized due to post-deposition oxidation in the ambient air. Oxygen was even diffused in an oxygen-bound layer, which was confirmed by repeated XPS depth profiling within three months after multilayer deposition. The upper oxygen-bound layer at the multilayer surface behaved as a barrier reducing oxygen diffusion. The high energy-resolution XPS spectra (C 1s, Si 2p, and O 1s) were analyzed to gain more insight into bonding species formed in functionally nanostructured film. This detailed analysis showed that oxygen atoms, originating from the ambient air, were bound in oxidized (a-CSi:H) layers forming the same bonding states as those in as-deposited oxygen-bound layers.

4:40pm **TF+SS-TuA8 Studying Electron Induced Chemical Changes of Hafnium Oxide-Methacrylate EUV Photoresists with *In Situ* IR Spectroscopy and Model Flat Surfaces**, ***Yasiel Cabrera,*** *E. Mattson, K. Oyekan, Y. Wang, Y.J. Chabal,* University of Texas at Dallas

New development in extreme ultraviolet (EUV) photolithography, using 13.5 nm photons, has brought us closer to a new era of device fabrication with sub-10 nm nodes. In the last decade, there has been many significant contributions to the development of EUV lithography, but limitations in photoresist development has made it difficult to implement the technology. Another significant challenge arises from the reality that EUV scanners are very expensive and limited for academia purposes, which ultimately slow down the process in understanding important mechanistic details for optimization of EUV resist materials. In this work, we emulate industrial EUV ionizing photons/events with low energy 90 eV electrons, which are believed responsible for inducing chemistry. Here, we are presenting results for nanoclusters resist based on hafnium-oxide core capped with methacrylic acid ligands (HfMAA). Using a combination of *in situ* infrared (IR) spectroscopy and density functional theory (DFT) calculations, we establish an atomic-scale mechanistic picture for each step of a photo-lithography process. To further understand the chemical changes leading to solubility switching, we have also developed a model surface system by translating the 3D structure considered in an HfMAA thin

films (< 30 nm thick on SiO_2) to a 2D system comprised of a single methacrylic acid (MAA) monolayer grafted onto an ALD grown HfO_2 film. The model system allows us to explore three areas related to the nanocluster system: first IR spectroscopy shows that the model surface is a good representation of the HfMAA thin film by matching many of the IR modes observed; second, similar to HfMAA, 90 eV electron irradiation shows the formation of alkyl CH_2 groups on the surface, with the loss of carboxylate and C=C bonds in the MAA adlayer; third, by comparing with different metal-oxide surface (Al_2O_3 and TiO_2) and different carboxylate ligands (isobutyric acid (IBA), and hydroxybenzoic acid (OHBA)), we have demonstrated that analogous metal oxide/adlayer combinations can be used as a comparative tool to survey optimal combinations of organic and inorganic compounds for resist development by quantitatively evaluating the role of metal centers in inducing reactions.

5:00pm **TF+SS-TuA9 Photoactivated Molecular Layer Deposition of Fluoropolymer Thin Films***, **Richard Closser**,* Stanford University*; M. Lillethorup,* Radisurf Aps, Denmark*; D.S. Bergsman, J. Shi, S.F. Bent,* Stanford University

Recent developments of organic thin-film technologies have highlighted the need for deposition techniques which allow for a high degree of control over film thickness and conformality. Many methods, such as chemical and physical vapor deposition, have made substantial progress towards meeting those requirements; however, molecular layer deposition (MLD) may be the ideal candidate for future development. MLD is an organic vapor deposition technique that takes advantage of sequential, self-limiting surface reactions, analogous to atomic layer deposition (ALD), whereby thin-film polymers can be deposited with angstrom-level thickness control even onto high aspect-ratio features. There are inherent constraints, however, to the variety of chemistries available for MLD, due to its vapor-phase nature, which precludes the use of solvents and many catalysts. As a result, most MLD polymers contain heteroatom-type connectivities and do not include new carbon-carbon bonding moieties, thus preventing the formation of many of the most common commercially available polymers.

Here, we discuss a new approach to MLD, photoactivated molecular layer deposition (pMLD), a process which provides new pathways to forming carbon-carbon bonds. In pMLD, monomers are activated upon exposure to UV light to create metastable radicals, which are then reacted with alkenes in a step-wise polymerization. Self-limiting bifunctional precursors are chosen which limit the extent of homopolymerization while enabling layer-by-layer growth. In this work, an alternating hydrocarbon-fluorocarbon polymer was deposited via pMLD using bifunctional diiodofluoroalkanes and dienes. It was determined using ellipsometry that the deposition has a constant growth rate and displays saturation behavior. X-ray photoelectron spectroscopy (XPS) analysis indicates the formation of new carbon-carbon bonds. By using alternate monomer backbones, we show that the composition follows a nearly 1:1 monomer deposition ratio, an indication that homopolymerization is minimized. In situ XPS annealing shows the fluoropolymer exhibits high temperature stability up to 400 ºC, similar to a pure polytetrafluoroethylene polymer. The films also display chemical resistivity to a variety of solvents, acids, and bases. Elemental mapping using Auger electron spectroscopy confirms that the fluoropolymer film can be patterned using a UV photomask. We also show that the pMLD film can be used for ALD inhibition, blocking up to 100 cycles of Pt ALD. The strategy described in this work enables a new scope of applications for MLD, whereby carbon-carbon bonds are formed, greatly expanding the MLD toolbox.

5:20pm **TF+SS-TuA10 Sputter-Deposited Porous Coatings for Solid Phase Microextraction***, **Tuhin Roychowdhury**, D.I. Patel, M.R. Linford,* Brigham Young University

Solid Phase Microextraction (SPME) is 'green method' for isolating target analytes from complex matrices. It works by placing a coated fiber near a sample such that the molecules of interest can be selectively extracted and concentrated. These captured species are then released into a chromatograph for separation, identification, and quantification. Popular, commercial SPME coatings suffer from various drawbacks that include solvent incompatibility, low capacity, limited lifetime, etc. These problems are addressed by our new class of SPME fibers that offer extraordinary capacity, sensitivity, and speed. Our approach includes sputtering silicon onto fiber substrates to produce columnar structures. These porous silicon nanostructures are further oxidized leading to a high density of silanol groups on their surfaces. We have now demonstrated that both silanes and ultrathin PDMS layers can be deposited on these surfaces. These coatings can be produced in various morphologies and thicknesses by manipulating the sputter and deposition conditions. For example, refractory materials like carbon can also sputtered onto these fibers to create porous morphologies, which should be beneficial for chromatography. The surfaces and materials generated for SPME in this project have been characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), spectroscopic ellipsometry (SE), time-of-flight secondary ion mass spectrometry (ToFSIMS), and wetting . The performance of our 2 µm thick, porous, sputtered coatings has been compared to that of a thicker (7 micron) commercial coating. Our fiber consistently outperforms the commercial fiber, showing significantly higher capacity for higher molecular weight polycyclic aromatic hydrocarbons (PAHs). PAHs are a significant environmental pollutant due to their toxicity and carcinogenicity. These results are not the end of what is possible. Based on our work in this area we are convinced that further significant improvements in extraction efficiency and selectivity are possible.

5:40pm **TF+SS-TuA11 Interfacial Electron Transfer of Ferrocene Immobilized onto Indium Tin Oxide through Noncovalent Interactions***, **Caitlin Hanna**, J. Yang,* University of California, Irvine

Immobilization of molecular species onto electrode surfaces is a strategy for the modification of surface properties with molecular specificity. Attachment of molecular fuel forming catalysts to photovoltaic electrodes, for example, is a promising route to efficient solar fuel generation. Current attachment methods are synthetically difficult and can have adverse effects on the electrode performance. This report describes a non-covalent method for molecular immobilization onto indium tin oxide (ITO) surfaces. The fabrication, characterization, and electrochemical behavior of 1-pyrenylferrocene physisorbed onto ITO surfaces through π-π interactions is described. X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry confirm the attachment of 1-pyrenylferrocene to the surface and highlight the stability of the system for aqueous electrochemical applications. The electron transfer kinetics between the ITO electrode and non-covalently attached ferrocene are compared to the kinetics of covalently-bound ferrocene. The kinetic studies of electron transfer show that electron transfer is ten times faster for non-covalently attached ferrocene than for covalently attached ferrocene.

6:00pm **TF+SS-TuA12 Vapor Phase Infiltration of Polymers with Intrinsic Microporosity: Structure and Chemical Separation Performance***, **Mark Losego**, E.K. McGuinness, F. Zhang, R. Lively,* Georgia Institute of Technology

Over 10% of the world's energy consumption goes to separating chemicals via thermal distillation. Membrane-based separation can drastically reduce these energy and financial costs, but membranes must be carefully designed to meet performance and durability needs. Polymers of intrinsic microporosity like PIM-1 are emerging membrane materials of interest for industrial separations. These materials can be readily formed into films and/or fiber bundles for rapid chemical separation. However, PIM-1 swells in many solvents (e.g., ethanol) and can suffer from long-term porosity collapse. We have been investigating the vapor phase infiltration of these PIM-1 materials with inorganic constituents to improve performance and long-term stability. These studies have revealed a number of surprising observations including that these materials can be loaded to an excess of 30 wt% inorganics using a single VPI exposure dose despite no indication of chemical binding between the organic and inorganic constituents. We currently believe this loading is due to an intermediate binding state between the metalorganic precursors and the PIM-1's nitrile group. This binding state is sufficiently stable to withstand 2 days of inert gas purging, yet when exposed to an oxidant and removed from the reaction chamber no permanent chemical reactions between inorganic and PIM-1 can be detected by XPS, NMR, or FTIR. After infiltration, these organic-inorganic hybrid membranes show unprecedented performance for a PIM, fully capable of separating small molecules in ethanol solvents that should swell and collapse the polymer's pores.

Thin Films Division
Room 102A - Session TF+EM+MI-WeM
Thin Film Processes for Electronics and Optics I

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

8:00am **TF+EM+MI-WeM1 Crystalline Conductors: Transition Metal Nitride Materials and Device Applications**, ***David Meyer**, D.S. Katzer, N. Nepal, B.P. Downey, M.T. Hardy, D.F. Storm,* U.S. Naval Research Laboratory **INVITED**

Development of gallium nitride and related III-N materials thin film growth technology has been instrumental in realizing high performance light-emitting, RF, and power electronic devices for both commercial and military applications. To continue pushing the frontiers of nitride materials research, we have recently incorporated a multi-pocket electron-beam evaporator into our nitride molecular beam epitaxy growth system to enable the evaporation of refractory transition metals. In spite of the complexity of the equilibrium phase diagrams of transition metal nitide (TMN) compounds, we have found that it is possible to grow single-phase TMN thin films epitaxially on SiC and AlN by carefully managing growth kinetics. This talk will discuss our latest results involving TMNs, such as NbN_x and TaN_x, which can be nearly lattice-matched and integrated within III-N heterostructures. Cross-sectional transmission electron microscopy indicates that TMN/III-N interfaces are atomically abrupt with no evidence of interdiffusion of the host elements. We anticipate that the device applications of these metallic films are quite broad ranging from selective etching of sacrificial layers for epitaxial lift-off of processed devices, to buried metallic or superconducting electrodes for quantum computation circuit elements, to optical mirrors and waveguides for improved optoelectronics.

8:40am **TF+EM+MI-WeM3 Growth Mechanism and Characteristics of Hf-Si-O Film by PE-ALD using TDMAS and TDMAH Precursors and Oxygen Plasma Gas**, ***Toshihide Nabatame**,* National Institute for Materials Science (NIMS), Japan*; M. Inoue,* National Institute for Materials Science (NIMS)*; E. Maeda, K. Yuge, M. Hirose,* Shibaura Institute of Technology, Japan*; M. Takahashi, K. Ito,* Joining and Welding Research Institute, Osaka University, Japan*; N. Ikeda,* National Institute for Materials Science (NIMS), Japan*; T. Ohishi,* Shibaura Institute of Technology, Japan*; A. Ohi,* National Institute for Materials Science (NIMS), Japan

GaN-based power devices with metal-oxide-semiconductor (MOS) structure have been widely investigated for next-generation power devices. To reduce the leakage current, Hf-Si-O has one candidate material among various gate insulators. To fabricate Hf-Si-O film, a HfO_2/SiO_2 laminate film was generally deposited by ALD. The growth mechanism of SiO_2 films was greatly changed by the oxidant gas when Tris(dimethylamino)silane (TDMAS) was as precursor [1]. By using ozone gas, the stable growth rate and high quality SiO_2 films could be obtained while no growth using H_2O gas. We expect that similar data can be also obtained by using oxygen plasma gas. However, the growth mechanism of the SiO_2 film during HfO_2/SiO_2 laminate film deposition and its characteristics have not been fully understood.

In this study, we systematically investigate growth rate of HfO_2/SiO_2 laminate film by plasma-enhanced ALD (PE-ALD) using TDMAS and Tetrakis(dimethylamino)hafnium (TDMAH) precursors and oxygen plasma gas, and also examine characteristics of the Hf-Si-O films.

The HfO_2/SiO_2 laminate films were deposited on SiO_2/Si substrates by PE-ALD at 300 °C with TDMAH and TDMAS precursors and oxygen plasma gas. The composition Hf/Si ratio of the HfO_2/SiO_2 laminate films were varied by changing each number of ALD cycle. The SiO_2 film was also deposited on SiO_2/Si and HfO_2/Si substrates by the same PE-ALD condition. The Hf-Si-O films were formed by post-deposition annealing (PDA) at 700 – 900 °C in a N_2 atmosphere. The growth per cycle (GPC) of the HfO_2/SiO_2 laminate, HfO_2, and SiO_2 films was estimated by spectroscopic ellipsometry, XPS, and cross-sectional TEM measurements. The structure of Hf-Si-O films was identified by XRD analysis, and electrical characteristics of capacitors with Hf-Si-O films were examined using capacitance – voltage measurement.

The GPC of the HfO_2/SiO_2 laminate, HfO_2, and SiO_2 films on SiO_2/Si substrates were found to be 0.08, 0.08, and 0.04 nm/cycle, respectively, regardless of Hf/Si composition ratio. Considering to the GPC of the HfO_2 (0.08 nm/cycle), the estimated GPC of a SiO_2 layer during HfO_2/SiO_2 laminate film deposition was 0.08 nm/cycle, which was unexpected, but increased by about 2 times compared to that of SiO_2 film on SiO_2/Si substrate. This suggest that an initial adsorption of TDMAS precursor on the SiO_2 and HfO_2 films must be different and strongly affects to the GPC. The Hf-Si-O films (Hf/Si=2/1) maintains amorphous structure even after PDA temperature at 900 °C. The Hf-Si-O films (Hf/Si=2/1) exhibited high dielectric constant of around 14 as expected.

Reference

[1] L. Han, and Z. Chen, ECS J. of Solid Sate Sci. and Technol., 2 N228 (2013).

9:00am **TF+EM+MI-WeM4 Atomic Layer Epitaxy of Ultra-wide Bandgap Ga_2O_3 Films**, ***Virginia Wheeler**, N. Nepal,* U.S. Naval Research Laboratory*; L.O. Nyakiti,* Texas A&M University*; D.R. Boris, S.G. Walton, B.P. Downey, D.J. Meyer,* U.S. Naval Research Laboratory*; C.R. Eddy, Jr.,* U. S. Naval Research Laboratory

Ga_2O_3 has emerged as a promising material for next generation power electronics and UV photodetectors applications due to its large bandgap (4.9 eV) and the availability of affordable native substrates from melt-grown bulk crystals. While β-Ga_2O_3 (monoclinic) is the most stable and studied of five polymorphs, the slightly less energetically favorable α- and ε-Ga_2O_3 phases have unique characteristics that can be exploited. The α-Ga_2O_3 (rhombohedral corundum) has the largest bandgap of 5.3 eV and can be alloyed with α-Al_2O_3 and α-In_2O_3 for bandgap engineering. T he ε-Ga_2O_3 phase (hexagonal wurtzite) is a polar phase, with a calculated polarization strength that is 10 and 3 times larger than that of GaN and AlN, respectively. Like the III-N system, polarization induced charges can lead to higher charge densities and mobilities in two-dimensional electron gases formed at heterojunctions, which would improve the viability of Ga_2O_3 electronic devices. In this work, we use atomic layer epitaxy (ALEp) to produce high-quality homo- and heteroepitaxial Ga_2O_3 films and investigate phase selectivity as a function of substrate type and orientation, growth temperature (T_g), plasma gas phase chemistry and gas pressure.

All ALE Ga_2O_3 films were deposited in a Veeco Fiji G2 reactor equipped with a load lock and turbo pump using trimethygallium and O_2 plasma precursors. Initial studies on c-plane sapphire substrates showed that decreasing chamber pressure an order of magnitude during the plasma step resulted in a shift from pure β-Ga_2O_3 to pure α-Ga_2O_3. Additionally, at 350°C and 8 mTorr, the phase could be altered by a varying the O_2 plasma flow from 5-100 sccm. Optical emission spectroscopy indicate that the ratio of O*/O2 is critical for phase selectivity while the high ion flux to the surface can contribute to the crystallinity at low T_g. By varying T_g from 300 to 500°C at 8 mTorr, films went from mixed β/ε phase at <350°C, to pure α-Ga_2O_3 at 350°C, to pure β-Ga_2O_3 at 500°C. Using the optimum growth conditions for α-Ga_2O_3 on c-sapphire, the influence of substrate was explored using a variety of substrates including AlN, GaN (bulk and epilayers), SiC, diamond, and Si. Deposition on III-N and β-Ga_2O_3 substrates all resulted in crystalline β- Ga_2O_3 films, while amorphous films were deposited on both SiC and Si. This suggests that a clean crystalline substrate interface is critical to obtaining high quality films and promoting metastable phases is more dependent on growth parameters than underlying crystal symmetry. Finally, we will discuss simple electrical properties of optimum films of each phase to validate feasibility of the process in device applications.

9:20am **TF+EM+MI-WeM5 Effects of Process Gases and Gate TiN Electrode during the Post Deposition Anneal to ALD-Al_2O_3 Dielectric Film**, ***Masaya Saito**, A. Teramoto, T. Suwa, K. Nagumo, Y. Shiba, R. Kuroda, S. Sugawa,* Tohoku University, Japan

We investigated effects of a post deposition anneal(PDA) to Al_2O_3 film which was formed by the low temperature atomic layer deposition(ALD)(1). Al_2O_3 films were formed at 75°C by the ALD process using $Al(CH_3)_3$ as a precursor and H_2O as an oxidant, and these thicknesses were 40 nm. TiN films were formed as gate electrodes of MIS capacitors. We applied three kinds of PDAs. N_2 and O_2 annealing at 400°C were applied just after the ALD(PDA Ⅰ(a), (b)), and N_2 annealing at 400°C was applied after the gate electrode formation (PDA Ⅱ). We measured C-V and I-V characteristics.

The negative V_{FB} compared to the ideal one(+0.54 V) was observed in the C-V curve without PDAs, and the fixed charge density calculated from V_{FB} was ~10^{13} cm^{-2}. In contrast, positive V_{FB} compared to the ideal one was observed in the C-V curve with PDA Ⅰ(b), and the fixed charge density was ~10^{11} cm^{-2}. These results indicate that PDA Ⅰ(b) is effective to decrease the fixed charges. Moreover, the hysteresis in the C-V curve decreased by PDA Ⅰ(b), and the leakage current also decreased within the voltage range of C-V measurement. It is considered that the decrease of hysteresis was caused by decreasing the electrons that were trapped in the Al_2O_3 film(2). However, a few samples broke down at low voltage after PDA Ⅰ(b). In contrast, we

couldn't measure the C-V characteristics of almost capacitors with PDA Ⅰ(a) because the capacitors broke down at low voltage. In the case of PDA Ⅱ which means N_2 annealing after the gate electrode formation, the leakage current decreased same as PDA Ⅰ(b) and the production yield was still good even after PDA Ⅱ This was different tendency from PDA Ⅰ(a) even as the same annealing. However, V_{FB} shifted to the positive voltage by the PDA Ⅱ and the fixed charge density was ~10^{12} cm^{-2}. This was the same phenomenon as the PDA Ⅰ(b).

We considered these phenomena as follows; the oxidizing species were desorbed by PDA just after the ALD, and then the film quality was bad after the N_2 annealing. The oxygen for improving the film was supplied by the O_2 annealing with the desorption. When PDA was carried out after the gate electrode formation, the desorption did not occur because of capping by the gate electrode, and then the oxidizing species were sufficient for improving the film by the annealing.

Reference:

(1) Y. Koda, et al., *ECS Trans.*, **72**(4), 91-100 (2016)

(2) L. Sambuco Salomone, et al., *J. Appl, Phys*., **123**, 085304 (2018)

Acknowledgement:

This work was carried out at fluctuation free facility of New Industry Creation Hatchery Center, Tohoku University.

9:40am **TF+EM+MI-WeM6 Controlling the NbO_xMaterials System for Neuromorphic Computing**,
Alexander C. Kozen, U.S. Naval Research Laboratory*; Z.R. Robinson, A.H. Rowley,* The College at Brockport - SUNY*; T.J. Larrabee, M.E. Twigg, H.S. Cho, S.M. Prokes,* U.S. Naval Research Laboratory

The niobium oxide system has seen recent interest, particularly due to its potential use as both a non-volatile, in the case of Nb_2O_5, or volatile, in the case of NbO_2, memristor material. Nb_2O_5 is a high k dielectric (k~41) with a high refractive index (n~2.2) and a wide bandgap (3.5 eV), while NbO_2 is a thermochromic material with a lower bandgap (1.2 eV) that undergoes a first order crystalline phase transition at a critical temperature (T_c) of 800˚C. Both of these phases, along with their intermediate sub-oxides, can serve as material components of memristors to facilitate low-power neural computing hardware.

We will examine the impact of annealing temperature, duration, and atmospheric chemistry on the phase selectivity of the NbO_x thin films fabricated using atomic layer deposition. Anneals of stoichiometric amorphous Nb_2O_5 films are kinetically limited by both Nb^{5+} to Nb^{4+} reduction and crystallization steps, and we find that the addition of H_2 during annealing is critical for the Nb^{5+} to Nb^{4+} reduction. To remove this kinetic-limiting step, we instead deposit reduced amorphous NbO_2 films, which crystallize at lower temperatures. We investigate the optical and electrical properties of both amorphous and crystalline NbO_x films and discuss the utility of the NbO_x materials system to the fabrication of memristor materials.

11:00am **TF+EM+MI-WeM10 Sputtering Power Dependent on Switching Characteristics of ZnO-based Transparent Resistive Memory Devices***,*
Firman Mangasa Simanjuntak, Tohoku University, Japan*; T. Ohno,* Oita University, Japan*; S. Samukawa,* Tohoku University, Japan

Transparent resistive random access memory (T-RRAM) devices have great potential as data storage for invisible electronics.[1] ZnO material is one of the promising candidates for T-RRAM application due to its high transparency to the visible light.[2] However, ZnO is an *n*-type semiconducting material which the intrinsic donor defects exist abundantly; consequently, the ZnO-based switching devices require high current compliance to operate as compared to another oxide system .[1,3] The employment of the high current compliance is to facilitate the formation of conducting filament. Various efforts have been made to improve the ZnO-based switching memories, such as: by controlling the thickness, introducing a dopant(s), adjusting the gas ambient during deposition, stacking with various material(s) and structure(s).[1] However, modulating the switching characteristics by controlling the sputtering power is still less overlooked. In this work, we investigated the influence of sputtering power in resistive switching characteristics of ZnO-based T-RRAM devices.

An approximately 50 nm thickness of ZnO films were deposited onto Indium Tin Oxide (ITO)-coated transparent substrates using conventional RF sputtering. Various sputtering power was used for the deposition while Ar/O_2 ambient is maintained at 2/1 ratio. The deposition rate was measured using a surface profilometer. In order to fabricate sandwich device structure, circular gallium-doped ZnO (GZO) top electrodes were deposited onto the ZnO/ITO structure; patterned using a metal shadow mask with 150 µm in diameter. X-ray diffraction and X-ray photoelectron spectroscopy were used to investigate the crystal structure and the defect concentration of the ZnO films, respectively. A semiconductor device analyzer was used to measure the electrical characteristics of the devices.

XRD pattern indicated that all ZnO films show (002) oriented crystals. The devices made with higher sputtering power showed lower leakage current for OFF state and lowered current compliance to form the conducting filament (for ON state). We also found that the donor defects (oxygen vacancies and zinc interstitials) decrease as the sputtering power increases. These findings indicate that the sputtering power parameter cannot be simply overlooked in the T-RRAM fabrication.

References

[1] F.M. Simanjuntak, D. Panda, K. Wei, and T. Tseng, Nanoscale Res. Lett. **11**, 368 (2016).

[2] F.M. Simanjuntak, O.K. Prasad, D. Panda, C.-A. Lin, T.-L. Tsai, K.-H. Wei, and T.-Y. Tseng, Appl. Phys. Lett. **108**, 183506 (2016).

[3] T. Ohno and S. Samukawa, Appl. Phys. Lett. **106**, (2015).

11:20am **TF+EM+MI-WeM11 Influence of Iintrinsic and Extrinsic Dopants in HfO_x Films for Resistive Switching Memory***,*
SungYeon Ryu, *Y. Kim,* Seoul National University of Science and Technology, Republic of Korea*; W.Y. Park, S.G. Kim,* SK Hynix Inc., Republic of Korea*; B.J. Choi,* Seoul National University of Science and Technology, Republic of Korea

Bipolar type resistive switching random access memories (RRAMs) utilized by TaO_x and HfO_x as switching materials, have been demonstrated superior to unipolar type RRAMs owing to the low switching current and better reliability. Bias-polarity-dependent valence change mechanism in HfO_x is attributed to the repeated generation and rupture of conducting filaments (CF), which could be the clusters of oxygen vacancies (V_o). As the device size scales down to 2x nm, the dimension of CF and the whole device area become comparable, and thus the involvement of oxygen loss or unintended V_O incorporation, that is, intrinsic defects may significantly degrade the device reliability. On the other hand, extrinsic defects by doping metallic elements may also change the switching characteristics and device variability depending on the fabrication methods, such as, co-sputtering, implantation, thermal and photo-assisted diffusion, etc.

In this study, influence of both intrinsic and extrinsic defects was investigated systematically. The device having TiN contact-plug with 28 to 2000-nm-diamenter formed in SiO_2 inter-layer was fabricated. 1.2-nm-thick HfO_x layer was deposited by atomic layer deposition (ALD). At first, for the control of intrinsic defect, the fabricated RRAM devices were post-annealed in both air and vacuum (~10mTorr) at a wafer temperature of 150 to 250 ^oC for 20 min, respectively. Electrical property is measured by semiconductor parameter analyzer (HP-4155) and function generator (AFG-3102) for DC and AC measurements. More reliable switching and free-from abnormal switching behavior, such as reset-failure, were observed in the vacuum-annealed device.

Secondly, Al- and Ga-doped HfO_x films are grown by using thermal ALD to change the structural and chemical properties of HfO_2 film via incorporating extrinsic defects. Dopant concentration and location were controlled by the ALD cycle ratio and sequence. Through Al doping, pristine resistance and forming voltage of the device were increased with increasing Al cycle ratio. On the other hand, Ga-doped HfO_2 device showed reverse switching polarity. The resistive switching characteristics caused by intrinsic and extrinsic defects in HfO_x films will be presented in detail.

Acknowledgment

This paper was result of the research project supported by SK hynix Inc.

11:40am **TF+EM+MI-WeM12 Scaling up of an Electrochemical Atomic Layer Deposition of Copper***,*
D. Dictus, Lam Research Corporation, Belgium*;* ***Aniruddha Joi,*** Lam Research Corporation*; G. Alessio Verni,* Lam Research Corporation, Belgium*; K. Vandersmissen,* Imec, Belgium*; B. Frees,* Lam Research Corporation, Belgium*; Y. Yezdi,* Lam Research Corporation

Just like atomic layer deposition in the gas phase, electrochemical atomic layer deposition in the liquid phase holds the promise of delivering very good conformality and uniformity for nm-thick film deposition by using surface limited reactions. Up to today however, there is no industry in which such process has been scaled up from cm-size coupons to industrial-scale substrates. In this paper, the scale up of electrochemical ALD of Cu is reported and it is demonstrated that this process can be used to fill <20 nm Cu interconnect lines as required for future microchip technology nodes.

The e-ALD process is a cyclic process that consists of a step in which a monolayer of Zn is deposited at a potential below the one, at which, Zn would grow multilayers (underpotential deposition), followed by a step in which the zinc is spontaneously displaced by Cu when the substrate is allowed to drift to the open circuit potential (surface limited replacement reaction, SLRR). By cycling between potentiostatic Zn deposition and open-circuit steps, Cu films can be grown in layer-by-layer fashion.

In contrast to classical electroplating processes, e-ALD processes do not require significant overpotential to create uniform nucleation. Also, current densities are small since the deposited amount of material per cycle is low. Therefore, the e-ALD process can be used to deposit Cu with atomic layer thickness control on substrates with high resistivity which gives the advantage of being able to plate on very thin (sub-20 A) liner materials.

Development of the e-ALD process is done on a Sabre electroplating tool from Lam Research on 300 mm substrates. These substrates contain a thin layer of Ru or Co on which the copper is deposited. The e-ALD process forms the seed layer for further metallization of the interconnect or can by itself fill the narrow interconnect lines.

We will demonstrate that good thickness uniformity can be achieved on 300 mm substrates with initial sheet resistance up to 1000 Ohm/sq and that filling of interconnect lines with dimensions smaller than 14 nm is achieved. Test chips containing our new Cu deposition process show high yield and the Cu interconnect lines have low resistance. This demonstrates the potential use of this new production method in future technology nodes.

12:00pm **TF+EM+MI-WeM13 A Novel High-deposition-rate PECVD Process based on Hollow Cathode Plasma Technique***, S. Shayestehaminzadeh, N. Rivolta,* AGC Glass Europe, Belgium*; M. Datz,* Interpane E&B GmbH*; **John Chambers**,* AGC North America*; H. Wiame,* AGC Glass Europe, Belgium

AGC Plasma has recently developed a hollow cathode plasma device as part of its activity as the industrial vacuum equipment manufacturing segment of AGC. This device has been successfully scaled up in order to perform the Plasma Enhanced Chemical Vapor Deposition (PECVD) processes for the coatings on the glass sizes ranging from a few square-centimeters up to a few square-meters (jumbo-sized glass plates 3.2 x 6.0 m^2). Plasma generation is undergone between multiple linear hollow cathode cavities, alternately driven by commercially available mid-frequency AC or pulsed power. This enables the generation of a dense and uniform plasma inside the cavities as well as outside of the cavities through the linearly located holes where a less dense plasma (as compared to inside the cavity) but still dense enough, can be utilized in order to activate the reaction between precursor and reactive gases in the depositing chambers. This geometry and condition allow the system to be scalable to relevant sizes for any typical vacuum processes.

The selected plasma generation method does not require magnets incorporated into the source. This will allow a simplified cooling system within the plasma source, as well as the possibility for adding other magnets to be positioned within the process chamber for modifying the plasma geometry. Based on plasma and vacuum simulations, the electrode-cavity design has been dramatically improved and can be driven by various gases, such as oxygen, nitrogen, argon, helium, and hydrogen. Plasma operation is also possible in an extremely wide range of pressures from 1 mTorr to 1 Torr, while the most useful process pressures for PECVD are generally in the 1 mTorr to 30 mTorr range. The wide hollow cathode pressure operation range allows for the deposition of multilayer coating stacks by magnetron sputtering and PECVD in the same vacuum coating lines.

Electrode faces have also been enhanced using surface coatings to avoid erosion during high power operation, also reducing subsequent debris and extending source lifetime. Depending on the choice of precursor materials, the desired film properties, and in-chamber magnetic field geometries, dynamic deposition rates for inline PECVD coatings of 200-500 nm*m/min have been demonstrated for SiO_2 on flat glass products however by selecting different gases and precursors various materials can be deposited using the same source line. This unique process opens a new range of possibilities to be investigated for a variety of substrates. These plasma sources are now commercially available in either lab or industrial sizes to explore new applications.

Biomaterial Interfaces Division
Room 104B - Session BI+AC+AS+HC+NS+SS+TF-WeA

Current and Future Stars of the AVS Symposium II

Moderator: David Boris, U.S. Naval Research Laboratory

2:20pm **BI+AC+AS+HC+NS+SS+TF-WeA1 Medard W. Welch Award Lecture: A Surface Scientist's Journey from Small Molecules to Biomolecules and Biomaterials*, David G. Castner*[1]*,*** University of Washington **INVITED**

Surface science plays an important role in a wide range of research and development areas such catalysis, biomaterials, microelectronics, clean energy and corrosion. The toolbox of surface scientist allows us to easily move across research topics and make significant impacts in both industrial and academic settings. The typical surface scientist is an expert in multiple techniques, surface modification, sample preparation/handling and instrumentation. We have all benefited from the significant and numerous advances that have occurred in the past 40 years in terms of improved instrumentation, introduction of new techniques and development of sophisticated data analysis methods, which has allowed us to perform detailed analysis of increasing complex samples. For example, comprehensive analysis of surfaces and surface immobilized molecules with modern surface science instrumentation provides an unprecedented level of detail about the immobilization process and the structure of the immobilized molecules. Results from x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), near edge x-ray absorption fine structure (NEXAFS), surface plasmon resonance (SPR) and quartz-crystal microbalance with dissipation (QCM-D) biosensing, atomic force microscopy, and sum frequency generation (SFG) vibrational spectroscopy combined with computation methods such as molecular dynamic (MD) and Monte Carlo (MC) simulations provide important information about surface chemistry and structure. However, even with the advances that have been achieved with these powerful surface science techniques, there still remain many significant challenges for surface scientist. These include characterizing the surface chemistry and structure of nanoparticles, determining the atomic level structure of complex molecules bound to surfaces, 3D imaging of samples, and improved sample preparation methods that maintain materials in a relevant state when using ultra-high vacuum based analysis techniques.

This talk will discuss my adventures as a surface scientist starting from chemisorption and reactivity studies of small molecules on single crystal surfaces followed by industrial catalysis research and eventually moving to biomedical surface analysis with side ventures into areas such as clean energy. It has been an exciting journey and I will use it to provide some examples of the multidisciplinary nature of surface science as well as discuss opportunities for addressing future challenges.

3:00pm **BI+AC+AS+HC+NS+SS+TF-WeA3 Invited Talk-Future Stars of AVS Session: Making, Studying, and Designing Hierarchically Structured Soft Materials*, Keith A. Brown*[2]*,*** Boston University

Nature realizes extraordinary materials by structuring them precisely from the molecular scale to the macroscopic scale. While nature may have perfected this process over evolutionary time scales, synthetically recapitulating this level of control is tremendously difficult due to the large number of length scales involved and our limited knowledge of interactions between these scales. Faced with the daunting challenge of synthetically realizing soft hierarchical materials, we have adopted a three pronged strategy to: (1) make structures with control from the molecular scale to the macroscopic scale by directing bottom-up growth processes with top-down control, (2) learn how the properties of such materials emerge from their hierarchical structure, and (3) design the best performing structures using novel approaches borrowed from machine learning and autonomous research. In this talk, we will on report recent progress in this complementary areas of making, studying, and designing hierarchical materials. In particular, we will focus on two major classes of materials, nanoparticle-based structures where the assembly and organization of particles leads to emergent mechanical properties at the bulk scale and polymer-based materials where we are connecting the synthesis, patterning, and properties of polymer structures across scales. In addition to lessons about the fundamental properties of hierarchically organized soft matter, we will highlight the synergies possible when combining, synthesis, detailed characterization, and advances in materials design.

3:20pm **BI+AC+AS+HC+NS+SS+TF-WeA4 Invited Talk-Future Stars of AVS Session: Vapor Phase Infiltration for Transforming Polymers into Hybrid Materials: Processing Kinetics and Applications*, Mark Losego*[3]*,*** Georgia Institute of Technology

Vapor phase infiltration (VPI) is an emerging processing technology for infusing polymers with inorganic constituents to create new organic-inorganic hybrid materials with novel chemical, electrical, optical, and/or physical properties. These new hybrid materials have demonstrated applications including chemical separations, photovoltaics, and microelectronics patterning. This talk will focus on our development of a fundamental VPI processing kinetics phenomenology to create a pathway for rational design of material composition and structure. By measuring VPI compositional profiles as a function of space or time and temperature, we can extract fundamental energy barriers for the sorption, diffusion, and reaction processes and delineate amongst different rate limiting steps. In our materials development, we often find that partial infiltration of a polymer film, fiber, or foam is sufficient to impart desired properties; so rational design of the infiltration kinetics can enable desired performance without waste in processing time or materials. Here, we will demonstrate several examples including our work to create chemically insoluble polymers and membranes. We find, for example, that infiltration depths of about 0.75 microns are sufficient to yield PMMA chemically insoluble in organic solvents regardless of whether it is in a thin film geometry or a macroscopic plexiglass object of centimeters in dimension. In PIM-1 membranes used for chemical separations, we find that we can achieve > 30 wt% inorganic loading with a single infiltration exposure. After infiltration, these membranes become stable in new separations solvents that previously swelled and/or dissolved the polymer.

(Submitted for the Future Stars of the AVS Symposium.)

4:20pm **BI+AC+AS+HC+NS+SS+TF-WeA7 Invited Talk-Future Stars of AVS Session: Surface Preparation Methods for the Selective Oxidation of Ethanol to Acetaldehyde over TiO_2/Au(111)*, Ashleigh Baber*[4]**, *D.T. Boyle, J. Wilke, V. Lam, D. Schlosser,* James Madison University

Obtaining a molecular-level understanding of the reaction of alcohols with heterogeneous model catalysts is critical for improving industrial catalytic processes, such as the production of hydrogen from alcohols. The use of reducible oxides provides a source of oxygen on Au(111) for the reaction of ethanol, which is easily regenerated in the presence of an oxygen background. The redox chemistry of small alcohols, including methanol and propanol, has been studied on Au(111) supported TiO_2 nanoparticles, yet the active site for the chemistry has not yet been elucidated. Depending on the surface preparation conditions, Au(111) supported TiO_2 nanoparticles react with small alcohols to form either reduced and oxidized products. The desire to selectivity form oxidized or reduced products merits an investigation of alcohol reactivity over differently prepared TiO_2/Au(111) surfaces. In this work, a systematic study of ethanol reactivity over several TiO_2/Au(111) surfaces elucidates the effect of surface conditions on the selectivity of the reaction between ethanol and TiO_2/Au(111). The reactivity of the surface for ethanol oxidation was altered by controlling the oxidation state of TiO_x (x<2). Atomic force microscopy (AFM) provides information regarding the structure of the Au(111) supported TiO_2 nanoparticles and ultrahigh vacuum temperature programmed desorption (TPD) monitors the selectivity of the reaction between ethanol and TiO_2/Au(111). The presence of TiO_2 nanoparticles on Au(111), ~25 nm in diameter, led to the catalytic conversion of ethanol to acetaldehyde at temperatures greater than 400 K. Low coverages of fully oxidized TiO_2 nanoparticles on Au(111) are active for the selective oxidation of ethanol to form acetaldehyde.

4:40pm **BI+AC+AS+HC+NS+SS+TF-WeA8 Invited Talk-Future Stars of AVS Session: Single Atom Catalysis: An Atomic-Scale View*, Gareth Parkinson*[5]*,*** TU Wien, Austria

Single-atom catalysis is a rapidly emerging area of research that aims to maximize the efficient usage of precious metals through "single atom" active sites. Although catalytic activity has been demonstrated for several single-atom catalyst systems, an inability to accurately characterize the catalyst based on single atom active sites ensures that that the field remains controversial, and little is really known about how a single atom

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

[2] **Future Stars of the AVS**

[3] **Future Stars of the AVS**

[4] **Future Stars of the AVS**

[5] **Future Stars of the AVS**

adsorbed on a metal oxide support catalyzes a chemical reaction. In this lecture, I will describe how we are addressing the crucial issues of stability and reaction mechanism using a surface science approach. The work is based on the magnetite (001) surface, which exhibits an unusual reconstruction based on subsurface cation vacancies.

The surface stabilizes ordered arrays of metal adatoms (of almost any variety) with a nearest neighbor distance of 0.84 nm to unprecedented temperatures as high as 700 K. Crucially, because the geometry of the adatoms is uniform and precisely known, reactivity experiments are performed on a well-defined model system, and theoretical calculations can be performed to shed light on the mechanisms at work. Several examples of our recent work will be used to illustrate the trends discovered to date, including how strong CO adsorption destabilizes Pd and Pt adatoms leading to rapid sintering, and how extraction of lattice oxygen from the metal-oxide is central to catalytic activity in the CO oxidation reaction.

5:00pm **BI+AC+AS+HC+NS+SS+TF-WeA9 Invited Talk-Future Stars of AVS Session: Multimodal Chemical and Functional Imaging of Nanoscale Transformations Away from Equilibrium**, ***Olga Ovchinnikova***[1], Oak Ridge National Laboratory

The key to advancing energy materials is to understand and control the structure and chemistry at interfaces. While much of the dynamic chemistry can be studied on macro-scale systems, there is a lack of means to localize chemical measurements and correlate them to nanoscale structure of the material. Through a unique merger of advanced scanning probe microscopy and mass spectrometry techniques rooted in innovative data processing and control algorithms, we are now able to understand the interplay between chemical and physical functionality at the fundamental length using multimodal chemical imaging. This multimodal imaging transcends existing techniques by providing nanoscale structural imaging with simultaneous quantitative nanomechanical properties and quantitative chemical analysis. In this talk I will discuss how we have developed and used this capability to visualize dynamic material transformations at interfaces, to correlate these changes with chemical composition, and to distil key performance-centric material parameters. One exciting capability is that the AFM can be used to drive materials away from equilibrium at the nanoscale with highly localized electric fields. This allows field confinement effects on localized chemistry in materials to be locally probed, especially at interfaces. This in turn yields direct information on key energy related questions such as electron and ion motion distribution and transport at and between interfaces. We have applied this approach to the study of systems and processes that underlie energy capture, conversion and storage, including photovoltaics and oxide ferroelectrics, which have historically eluded comprehensive understanding of the mechanisms behind the spatially heterogeneous interfacial chemistry and its link to material performance. Overall, I will focus on ways to unlock the mystery of active interface formation through intertwining data analytics, nanoscale elemental and molecular characterization, with imaging; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

5:20pm **BI+AC+AS+HC+NS+SS+TF-WeA10 Invited Talk-Future Stars of AVS Session: Expanding the Structural Toolkit to Characterize Heavy Actinide Complexes**, ***Rebecca Abergel***[2], Lawrence Berkeley Lab, University of California, Berkeley; *G. Deblonde, A. Mueller, P. Ercius,* Lawrence Berkeley National Laboratory; *A.M. Minor,* Lawrence Berkeley Lab, University of California, Berkeley; *C.H. Booth, W.A. de Jong,* Lawrence Berkeley National Laboratory; *R. Strong,* Fred Hutchinson Cancer Research Center

Structural characterization of actinide elements from actinium to einsteinium can be a challenging task due to the high radioactivity and limited availability of some of the isotopes of interest. However, significant work is needed to address a certain lack of understanding of the fundamental bonding interactions between those metal centers and selective ligands. Such understanding presents a rich set of scientific challenges and is critical to a number of applied problems including the development of new separation strategies for the nuclear fuel cycle, the need for decontamination after a nuclear accident or the use of radio-isotopes for new cancer treatments. Our studies utilize luminescence sensitization, UV-Visible, X-ray absorption, and X-ray diffraction spectroscopic techniques as well as transmission electron microscopy and electron energy loss spectroscopy to investigate specific heavy actinide coordination features. Using simple inorganic complexes but also strong hard oxygen-donor ligands as well as more elaborate higher molecular weight protein assemblies allows the differentiation of heavy actinide species even when limited to minute amounts of materials. Innovative structural characterization approaches based on X-ray absorption, X-ray diffraction and electron microscopy that were applied to series of isostructural systems and used to derive coordination trends in the later 5*f*-element sequence will be discussed.

5:40pm **BI+AC+AS+HC+NS+SS+TF-WeA11 Invited Talk-Future Stars of AVS Session: Trends in Adsorbate Interactions with Bimetal Surfaces**, ***Liney Arnadottir***[3], *L.H. Sprowl,* Oregon State University

Surface chemistry plays an important role in a large range of applications and technologies, such as catalysis and electrocatalysis, device fabrication through film growth, and degradations through oxide formation, carbonization, and corrosion. Bimetal surfaces are of increasing interest for single atom catalysis and corrosion resistance of alloys. Previous studies have shown correlations between adsorbate interactions and d-band shifts for different metals as well as for alloying effects of metal sandwich structures, but for mixed metal surfaces the nature of the adsorption site can change (ensemble effect) as well as the number of electrons in the surface layer which effects the d-band center. Here we explore correlations of adsorbate interactions with mixed metal surfaces through density functional theory calculations of adsorbate interactions with different facets, (100) and (111), of pure Ni and eleven Ni-based surface alloys as well as Ni in different host metal. We find that the addition of surface alloying atom has little effect on the binding of CO and C but C binding varies for different facets. On the other hand, O binding is highly dependent on the alloying element due to ensemble effect. This has an interesting effect on the predicted reaction energies of CO dissociation which is endothermic on the (111) facet and exothermic on the (100) facet governed by C interactions but the changes in the reaction energy within each facet are mostly governed by the ensemble effect on O adsorption. The relationship between the formation energy of the mixed metal surface and adsorbate interactions will also be discussed.

Thin Films Division
Room 102A - Session TF+EM+MI-WeA

Thin Film Processes for Electronics and Optics II

Moderators: Hilal Cansizoglu, University of California, Davis, John F. Conley, Jr., Oregon State University

2:20pm **TF+EM+MI-WeA1 What can we Benefit from Nanochemistry of Crystalline Silicon?**, ***Naoto Shirahata***, National Institute for Materials Science, Tsukuba, Japan **INVITED**

The richly tunable optical properties of colloidal silicon nanoparticles, in conjunction with flexible functionalization of their surfaces, makes them important class of materials with various potential applications in the ranging from medicine to optoelectronics. Bulk crystal of silicon is an indirect bandgap semiconductor, resulting in poor light emission and a weak absorption onset – major technological barrier for their use in photonics. The successful approaches in transforming silicon into efficient light emitters are appearance of the quantum confinement effect and reformation in atomic structure and periodicity from diamond cubic lattice to nanoclusters having a direct gap structure. The improved optical properties including photoluminescence quantum yields, require the efficient radiation recombination between photogenerated electron-hole pairs across the gaps. To achieve this, the surface chemistry plays an important role. In particular, the formation of carbon-silicon linkage at the surface of the nanoclusters results in the enhanced radiative recombination probability.

Today's talk starts by describing a brief overview of light emitting silicon nanoparticles to understand their place in the world of colloidal semiconductor nanocrystals. Next, the talk focuses on the reliable approaches to give a fine tuning of photoluminescence spectra with high spectral symmetries and impressively narrow spectral linewidths. Recent progress of chemical synthesis and surface functionalization of silicon nanoparticles is then demonstrated, in conjunction with their applications including efficient light emitting diodes and non-toxic biomarkers adapted for two-photon excitation fluorescence cell imaging. The performance of silicon-based light emitters are influenced significantly by surface moiety.

[1] **Future Stars of the AVS**
[2] **Future Stars of the AVS**
[3] **Future Stars of the AVS**

Since the finding of porous silicon in 1990, the free-standing, strongly luminescent silicon nanoparticles have become a masterpiece of nanoscience and nanochemistry. Such thermodynamically-stable colloidal nanoparticles will continue to lead to novel concepts of medical and device applications in near future.

3:00pm **TF+EM+MI-WeA3 Low-temperature Homoepitaxial Growth of Two-dimensional Antimony Superlattices in Silicon**, ***April Jewell**, M.E. Hoenk, A.G. Carver, S. Nikzad,* Jet Propulsion Laboratory

Our group has previously reported on the growth of antimony delta-doped silicon by low-temperature molecular beam epitaxy. In this presentation we will discuss the extension of our antimony delta doping capabilities to the growth of n-type superlattices (i.e. films that incorporate multiple delta layers). We will discuss details related to growth optimization, and show results from in situ monitoring by Auger electron spectroscopy and electron diffraction. We will also report on electrical characterization of our films and preliminary device measurements.

JPL's delta doping and superlattice doping (i.e., two-dimensional "2D" doping) processes have been developed primarily for use with silicon-based scientific imagers. A key performance metric for these detectors is photometric stability, a parameter that depends largely on passivation at the detector interface. Our approach uses an atomically thin (2D), highly concentrated layer of dopant atoms embedded within nanometers of the surface. This allows for dopant concentrations in the range of 10^{13}-10^{14} cm^{-2} (10^{20}-10^{21} cm^{-3}); higher than can be achieved with 3D doping techniques. Resulting quantum effects within the highly-doped 2D layers result in exceptional stability in 2D-doped devices.

N-type 2D-doping with antimony is challenging primarily because it tends to segregate to the surface. Segregation is suppressed at low temperatures; however, this may compromise epitaxial growth and lead to poor dopant incorporation and activation. Even so, it has been shown that at sufficiently slow silicon deposition rates it is possible to maintain epitaxial growth even at low temperatures for finite thicknesses. In our previous work with single n-type delta layers, we demonstrated activated dose concentrations as high as 2×10^{14} cm^{-2} and sharp dopant profiles (~35 Å FWHM). Under the current effort we have further optimized our growth processes to achieve even sharper dopant profiles and multiple delta layers. This is enabled by switching from a standard effusion cell to a valved cracker cell for antimony evaporation, which allows for high atom and carrier densities on the order of ~10^{21} cm^{-3} with peak distribution at ~10 Å FWHM.

The performance of our low-temperature 2D-doping processes has been validated by applying both p-type and n-type superlattice-doping to fully depleted photodiodes. The superlattice-doped devices show significantly higher responsivity than the equivalent ion-implanted devices. Additionally, when exposed to pulsed X-rays the superlattice-doped devices exhibit fast response and recovery times required for use in pulsed power experiments.

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4:40pm **TF+EM+MI-WeA8 Epitaxial Growth and Electrical Properties of VO_2Thin Films**, ***Yang Liu**, S. Niu, T. Orvis, H. Zhang, H. Wang, J. Ravichandran,* University of Southern California

We report the epitaxial growth and the electrical properties, especially the metal-to-insulator transition (MIT) of vanadium dioxide (VO_2) thin films synthesized on lanthanum strontium aluminate tantalate (LSAT) (111) substrates by a pulsed laser deposition method. X-ray diffraction study shows that the epitaxial relation between the VO_2 thin films and LSAT substrate is given as VO_2(020)||LSAT(111) and VO_2[001]||LSAT[11-2]. We observed a sharp change of four orders of magnitude in resistance at the MIT temperature of 345K. We measured distinctive Raman spectra below and above the transition point indicating a structural transition between the insulator and metallic phases, as observed in past investigations.

5:00pm **TF+EM+MI-WeA9 A Novel Technique for the Growth of Gallium Oxide Nanowires for UV Detection**, ***Badriyah Alhalaili**,* UC, Davis*; R.J. Bunk, H. Mao,* UC Davis*; R. Vidu,* UC, Davis*; H. Cansizoglu,* UC Davis*; M.S. Islam,* UC, Davis

Recently, high interest in wide bandgap semiconductors for a variety of applications has grown. Due to the unique thermal, optical, and electrical properties of Ga_2O_3, the scientists attract to the assessment of Ga_2O_3 nanowires (NWs) as a valuable material in semiconductor research fields, especially for applications in harsh environments and power electronics. Compared to thin films, nanowires exhibit a higher surface-to-volume ratio, increasing their sensitivity for detection. Additionally, nanowire devices exhibit quantum effects not seen in bulk materials and allow for crystalline materials to be grown on arbitrary substrates in spite of lattice mismatch due to lattice strain relaxation at the interface. In this work, we explore a simple and inexpensive method of growing high-density gallium oxide NWs at high temperatures. The gallium oxide NWs growth mechanism can be obtained by heating and oxidizing the gallium metal into high temperatures above 900 °C. This process can be optimized for large-scale production with high-quality, dense and long-length of gallium oxide NWs. We show the results of the characterization of the materials including the optical band gap, Schottky barrier height with metal contacts, and photoconductance of β-Ga_2O_3 nanowires. The influence of density on these Ga_2O_3 nanowires will be examined in order to determine the optimum configuration for the detection of UV light.

5:20pm **TF+EM+MI-WeA10 Enhanced Efficiency in Photon-trapping Ge-on-Si Photodiodes for Optical Data Communication**, ***Hilal Cansizoglu**, C. Bartolo Perez, Y. Gao, E. Ponizovskaya Devine, S. Ghandiparsi, K.G. Polat, H.H. Mamtaz, M.F. Cansizoglu,* University of California, Davis*; T. Yamada,* University of California, Santa Cruz*; A.F. ElRefaie, S.Y. Wang,* W&WSens Devices, Inc.*; M.S. Islam,* University of California, Davis

High speed, surface illuminated Ge-on-Si *pin* photodiodes with improved efficiency are fabricated and characterized. External quantum efficiency (EQE) of the Ge-on-Si *pin* diode is enhanced to >80% at 1300 nm and 73% at 1550 nm with only 2 µm thick intrinsic Ge layer, which is required to maintain high speed operation. Improved EQE is achieved by guiding incident light into the device structure with the help of microholes arranged in a lattice with a periodicity at the scale of wavelength. Vertically propagating light is coupled to the lateral modes in the material with periodic holes and absorbed efficiently despite a thin layer. More than 350% of EQE is enhanced by hole arrays compared to the case without holes up to 1700 nm wavelength. Such promising results enable Ge-on-Si photodiodes potentially cover both existing C band (1530 nm-1560 nm) and L band (1560 nm-1620 nm) and a new data transmission window (1620 nm-1700 nm), which can be a solution to capacity crunch of conventional standard single mode fiber (SSMF) cables. CMOS/BiCMOS compatible fabrication of photon-trapping Ge-on-Si photodiodes can lead to integrated transceiver circuits with electronics for cost-effective solutions in various near-infrared sensing applications such as metro and long haul dense wavelength division multiplexing (DWDM) systems, laser radar (LIDAR) systems, quantum communications and near-infrared imaging.

5:40pm **TF+EM+MI-WeA11 Correlating Composition and Structure with Optical Properties of Combinatorial Sputtered Thin Film Au_xAl_{1-x} Alloys**, ***Robyn Collette**,* University of Tennessee Knoxville*; Y. Wu, J.P. Camden,* University of Notre Dame*; P.D. Rack,* University of Tennessee Knoxville

Surface plasmon resonances can be sustained by metallic nanostructures and have been explored for potential optoelectronic device applications. Superior plasmonic properties may be realized by alloying and consequently tuning the LSPR, however, there has been limited work done on alloys for use in plasmonic devices. The alloy behavior greatly depends on the ordering of the structure; thus, it is crucial to explore how the optical properties are related to the structure of the alloy.

In this work, the structure and optical properties of Au-Al thin film alloys were investigated as both individual metals have strong plasmon resonances. Initially, 350 nm thick Au_xAl_{1-x} ($0.15<x<0.72$) was co-sputtered on 100mm x 15mm silicon substrates. Subsequently samples of $0.9<x<1$ and $0<x<0.2$ were investigated. Energy dispersive spectroscopy (EDS) was used to measure the composition as a function of position on the substrate for the combinatorial samples. The crystal structure at various compositions were subsequently determined using grazing incidence x-ray diffraction (GIXRD) and the dielectric constants, ε_1 and ε_2, were determined via spectroscopic ellipsometry. The evolution of phases was studied by annealing various compositions under vacuum and the optical properties were correlated to observed phases on the equilibrium phase diagram. Lastly, we explore the plasmonic properties of lithographically patterned Au_xAl_{1-x} ($0<x<0.2$). The optical transmission and reflection is measured and compared with electron energy loss spectroscopy results. The phase evolution is studied using a (scanning) transmission electron microscope with an *in situ* laser heating system and the low loss electron energy loss spectra are correlated to the structural changes. Interestingly, we found in the mixed phase region containing Al and $AuAl_2$ that as the concentration of $AuAl_2$ increased, an increase of ε_1 and a decrease of ε_2 around 1.5 eV.

6:00pm **TF+EM+MI-WeA12 The Multifunctional TiO2 Thin Films Sensor***,*
Awais Ali*, M. Alam, S. Nasser, N. Akbar, A. Saeed, A.S. Bhatti,* COMSATS Institute of Information Technology, Islamabad Pakistan

In the present work, multifunctional/hybrid UV and IR sensing was performed by Nd doped TiO_2 thin films. Thin films were sputter deposited and concentrations of dopants was varied in targets. The results suggested that the incorporation of Nd produced compressional stresses in lattice, which resulted in textured growth and asymmetry of bonds as confirmed by XRD and Raman spectroscopy. The dopant driven non-stoichiometry and presence of O vacancies was evident from XPS measurements. The defects and dopant mediated luminescence was obtained in visible and IR regions, respectively. The sensing of UV light was attributed to the host (titania), whereas successful incorporation of dopant helped in sensing IR source.

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

Atomic Layer Processing: Atomic Layer Etching

Moderators: Erwin Kessels, Eindhoven University of Technology, The Netherlands, Mingmei Wang, TEL Technology Center, America, LLC

8:00am **PS+EM+TF-ThM1 Precise Flux Control of Ions and Radicals using Electron Beam Generated Plasmas***, **David Boris,*** U.S. Naval Research Laboratory **INVITED**

Processing with atomic layer precision requires the ability to not only add, remove or modify one monolayer of material but to also leave adjacent layers unchanged. This requires fine control over the flux of species and energy deposition at the surface. In addition to the need for low damage, the complex device structures proposed for next generation nano-electronics will require control over radical to ion ratio as well. Electron beam-generated plasmas are generally characterized by high charged particle densities (10^{10}- 10^{12} cm^{-3}), low electron temperatures (0.3 - 1.0 eV), and in reactive gas backgrounds, a relatively low radical production rate compared to discharges. These characteristics provide the ability to precisely control the ion energy at adjacent surfaces and importantly, also the ability to control the ratio of ion to radical fluxes. In this work, we demonstrate this precise level of control using a variety of plasma characterization techniques and demonstrate how the applicability of these features to the processing of select materials systems. Specifically, we will discuss the processing of monolayer material systems such as graphene and MoS_2, where the material properties can be tuned without unwanted erosion or damage. Also SiN etching using pulsed, electron beam generated plasmas produced in SF_6 backgrounds is examined with particular attention paid to the etch rates, selectivity (vs. carbon films, Si and SiO_2), and patterning as function of operating parameters such as relative gas concentration, operating pressure, and substrate bias. Lastly, we address the use of electron beam generated plasmas for native oxide removal and subsequent passivation of surfaces. The processing results are compared with plasma diagnostics to gain a better understanding of the process requirements. This work is partially supported by the Naval Research Laboratory base program.

8:40am **PS+EM+TF-ThM3 Demonstration of Self-limiting Nature and Selectivity Control in Annealing Procedures for Rapid Thermal-Cyclic ALE of W, TiN, and SiN***, **Kazunori Shinoda**, H. Kobayashi,* Hitachi, Japan*; N. Miyoshi, K. Kawamura, M. Izawa,* Hitachi High-Technologies, Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Isotropic atomic layer etching (ALE) is expected to play an important role in semiconductor manufacturing because the next-generation devices will have miniaturized three-dimensional structures. The authors have developed isotropic ALE for SiN, TiN, and W using rapid thermal-cyclic processes, which are cyclic repetitions of plasma exposure and infrared annealing [1, 2]. Isotropic ALE ideally consists of cyclic repetitions of self-limiting formation and self-limiting desorption of the surface-modified layers. In the previous publications, the authors demonstrated self-limiting nature of the plasma exposure steps. In this paper, self-limiting nature of the infrared annealing steps are demonstrated. It is also demonstrated that etching selectivity between different materials can be controlled to be from infinitely selective to nonselective by adjusting the infrared annealing time.

The experimental apparatus used in this study is an ALE tool for 300-mm wafers. This tool is composed of a processing chamber, an inductively-coupled plasma source, infrared lamps, and in-situ ellipsometer. Films of W, TiN, and SiN deposited on Si substrates were used as sample materials. The wafers were first exposed to hydrofluorocarbon-based plasma to produce surface-modified layers on the surfaces of the materials to be etched. The wafers were then annealed by infrared irradiation to remove the surface-modified layers. The cycle of plasma exposure and infrared annealing was repeated ten times.

Firstly, infrared annealing time dependence of wafer temperature was examined. It was found that wafer temperature increased with increasing irradiation time at around 7°C /sec. Next, we examined how the annealing time affected the etched amount per cycle for W, TiN, and SiN. In the experiment, ten-cycle etching was repeated changing the annealing time in the range from 0 to 24 sec. The etched amount per cycle for W increased with the annealing time and saturated when the annealing time exceeded 10 sec. The etched amount per cycle for TiN increased when the annealing time exceeded 10 sec and saturated when the annealing time exceeded 20 sec. The etched amount per cycle for SiN saturated when the annealing time exceeded 15 sec. These results imply that the ALE process for W, TiN, and SiN are self-limiting in nature. Moreover, by choosing an optimal infrared annealing time, both highly selective and nonselective ALE for different materials was obtained. For instance, infinitely selective ALE of W over TiN was achieved when infrared annealing time was 8 sec.

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

[2] K. Shinoda et al., SPIE Advanced Lithography 10589-17 (2018).

9:00am **PS+EM+TF-ThM4 Mechanisms for Atomic Layer Etching of Metal Films by the Formation of Beta-diketonate Metal Complexes***, **Tomoko Ito**, K. Karahashi, S. Hamaguchi,* Osaka University, Japan

Ar^+ ion milling processes have been widely used for the fabrication of magnetic tunnel junctions (MTJ) of magnetoresistive random access memory (MRAM) devices. However, Ar^+ ion milling has a problem of surface damage caused by high energy ion bombardment, so the development oflow-energy reactive ion etching (RIE) processes is imperative for further miniaturization of MTJ cells. In recent years, beta-diketones such as acetylacetone (acac) andhexafluoroacetylacetone (hfac) have been considered as efficient etchants for thermal atomic layer etching (ALE) of metal films by the formation of volatile beta-diketonate metal complexes. Moreover, if low-energy ion incidence, rather than heating of the substrate, enhances the formation of organic metal complexes and their desorption from the metal surface, anisotropic ALE of metal films may be achieved. In this study, we explore the possibility of the development of such ion-enhanced metal surface etching using surface reactions of beta-diketones. The objectives of our research are, therefore, to understand surface reactions between gas-phase beta-diketones and metal surfaces and to clarify the beam-surface interaction between low-energy Ar^+ ions and beta-diketone adsorbed metal surfaces. To achieve these objectives, we have developed an atomic layer process (ALP) surface analysis system, which consists of a high-resolution X-ray photoelectron spectroscopy (XPS) analysis chamber and an ALP reaction chamber. The system allows *in-situ* analyses of, e.g., acac orhfac adsorbed Cu, Ni and Co surfaces and those after an exposure to low-energy Ar^+ or Xe^+ ion fluxes. The typical reactive gas exposure was in the range of 100 -10000 L (in units of L: Langmuir: 10^{-6} Torr・s) and the ion energy was in the range of 10- 50 eV. It is found that, for pre-oxidized Ni and Cu surfaces, hfac molecules adsorbed without C-O and C-F bond braking. It is also found that low-energy Ar^+ ion injection breaks down adsorbed hfac molecules even on a pre-oxidized Ni surface, fluorinating the Ni surface. The results show the difficulty of using low-energy ion exposure to enhance the formation of volatile metal complexes but also suggests a possibility of atomic-level surface modification of metal films using organic molecules, which may be used for highly controlled etching processes.

9:20am **PS+EM+TF-ThM5 Thermal Atomic Layer Etching of Transition Metal Films***, **Charles Winter,*** Wayne State University **INVITED**

Atomic layer deposition (ALD) features self-limited growth, which affords inherently conformal coatings on shaped substrates and Ångstrom-level thickness control.[1] Atomic layer etching (ALE) is a related technique, where layers in a film are removed one layer at a time and involve a self-limited mechanism.[2] Until recently, almost all ALE processes entailed either plasmas or ion beams.[2] Plasmas and ion beams require expensive equipment and the energetic species may damage sensitive layers in films. As a result, there is considerable interest in the development of purely thermal ALD processes that use chemical reactions to achieve thickness reductions. The first thermal ALE processes were only reported in 2015 for metal oxides and fluorides,[3-5] and many materials can now be etched thermally. Cobalt, copper and other first row transition metal films have wide applications in microelectronics devices.[6] The ability to carry out ALE on these metals would be very valuable. However, there has been little progress reported to date in the thermal ALD of first row transition metal films. We recently reported the ALD growth of cobalt[7] metal films and have explored these films as starting substrates in thermal ALE. In this talk, we will give an overview of the thermal ALE of cobalt metal films. These processes entail treatment of the cobalt metal films with formic acid in a first step, presumably to afford surface layers of cobalt(II) formate. These oxidized surfaces are then treated with various ligands in a second step to afford volatile cobalt(II) complexes, resulting in etching. Ligands that can be used to promote etching will be overviewed. Thermal ALE of copper and other metal films will also be presented.

1. S.M. George, Chem. Rev. 110 (2013) 111-131.

2. K.J. Kanarik, T. Lill, E.A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, R.A. Gottscho, J. Vac. Sci. Technol. A 33 (2015) 020802.

3. Y. Lee, S.M. George, ACS Nano 9 (2015)2061-2070. Y. Lee, J.W. DuMont, S.M. George, Chem. Mater. 27 (2015)3648-3657.

4. Y. Lee, J.W. DuMont, S.M. George, J. Phys. Chem. C 119 (2015) 25385-25393.

5. Y. Lee, J.W. DuMont, S.M. George, ECS J. Solid St. Sci. Technol. 4 (2015) N5013-N5022.

6. C.-C. Yang, P. Flaitz, P. Wang, F. Chen, D. Edelstein, IEEE Electron Dev. Lett. 31 (2010) 728-730.

7. M.M. Kerrigan, J.P. Klesko, C.H. Winter, Chem. Mater. 29 (2017) 7458-7466.

11:00am **PS+EM+TF-ThM10 Gas Cluster Ion Beam Etching under Organic Vapor for Atomic Layer Etching**, ***Noriaki Toyoda,*** University of Hyogo, Japan **INVITED**

In our presentation, we will present our investigation of the usage of a gas cluster ion beam (GCIB) under organic vapor to irradiate a surface to produce atomic layer etchings (ALE). Gas cluster ions are aggregates of thousands of atoms or molecules that are collectively ionized and can be focused into a GCIB. The kinetic energy of a gas cluster ion is shared between the thousands of gas atoms or molecules; hence, the energy per particle in the cluster can be easily reduced to several eV. Furthermore, gas cluster ions can transfer a relatively large amount of energy to a concentrated area of the target surface; thus, a large number of target atoms can be sputtered by one gas cluster ion. As a result of the high-energy impact of gas cluster ions, low-damage surface modification takes place. Because of the features outlined above, GCIB guns are also widely used in conjunction with surface analysis techniques such as secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS).

Because gas cluster ions deposit energy in a condensed manner without severe damage, surface reactions are enhanced even at room temperature, which is beneficial for ALE. In our study, we performed halogen-free ALE of Cu using oxygen-GCIB irradiation under acetic acid vapor [1]. We performed the etching process in the following steps: (1) adsorption of acetic acid on Cu, (2) evacuation of residual acetic acid vapor, and (3) reaction between acetic acid and Cu with the subsequent removal of the surface Cu layer via oxygen-GCIB irradiation. During one cycle of ALE, a very thin layer of acetic acid was adsorbed onto the Cu. Subsequently, the chemically altered Cu on the surface layer was removed with oxygen GCIB irradiation. When the Cu surface was irradiated with a 20 kV oxygen GCIB, Cu atoms beneath the surface layer were also sputtered after the removal of the chemically modified layer and as a result, this etching process was not self-limiting. On the contrary, when the surface was irradiated with a 5 kV oxygen GCIB, Cu atoms beneath the surface layer were not sputtered after the removal of the chemically modified layer. Thus, it could be concluded that halogen-free ALE could only be achieved at a lower oxygen GCIB voltage, namely 5kV. In the presentation, we will report the preliminary results of the various metal etching experiments we conducted with a GCIB under organic vapors and report their applications for ALE.

[1] N. Toyoda and A. Ogawa, Journal of Physics D: Applied Physics, 50, 184003 (2017).

11:40am **PS+EM+TF-ThM12 Utilizing Chemical Structure of Hydrofluorocarbon Precursors to Achieve Ultra-High Selective Material Removal in Atomic Layer Etching**, ***Kang-Yi Lin,*** *C. Li,* University of Maryland, College Park*; S.U. Engelmann, R.L. Bruce, E.A. Joseph,* IBM Research Division, T.J. Watson Research Center*; D. Metzler,* IBM Research Division, Albany, NY*; G.S. Oehrlein,* University of Maryland, College Park

Atomic layer etching (ALE) applies sequential deposition and etching steps with short processing step length to establish selective material removal and atomic scale precision. The reactant pulsed in the ALE sequential reaction steps may behave differently from its use in continuous plasma etching, since for ALE the reactant is injected only during the deposition step and the deposited film undergoes non-steady-state surface desorption reaction during the etching step. In this work we will compare a mixture of a fluorocarbon (FC) precursor and H_2 with a hydrofluorocarbon (HFC) precursor, i.e. mixtures of octafluorocyclobutane (C_4F_8) with H_2 and 3,3,3-trifluoropropene ($C_3H_3F_3$), for SiO_2 ALE and etching of SiO_2 selective to Si_3N_4, Si and SiGe. For continuous plasma etching, process gas mixtures, e.g. C_4F_8/H_2, have been employed and enable highly selective material removal based on reduction of the fluorine content of deposited steady-state HFC films. This approach, however, is not successful for ALE since the residual hydrogen during reaction steps will induce etching and reduce the remaining thickness of the deposited HFC film. This HFC film on the surface is required for both etching of SiO_2 and passivation of the Si_3N_4, Si and SiGe, and a reduction in film thickness leads to lower material etching selectivity. $C_3H_3F_3$ with hydrogen reduces fluorine content in the precursor structure and allows deposition of fluorine-deficient HFC films without suppressing the formation of the passivation layer on the surface. Our results support that gas pulsing of complex HFC precursors in ALE provides a novel opportunity of utilizing the precursor chemical structure for achieving near-atomically abrupt selective ALE processes for SiO_2 over Si_3N_4, Si, SiGe and potentially for other materials. The authors gratefully acknowledge financial support of this work by the Semiconductor Research Corporation (2017-NM-2726).

12:00pm **PS+EM+TF-ThM13 Etch Selectivity Mechanisms of Implanted Over Pristine SiN Materials in NH_3/NF_3 Remote Plasma for Quasi Atomic Layer Etching with the Smart Etch Concept**, ***Vincent Renaud,*** *E. Pargon, C. Petit-Etienne,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; J.-P. Barnes, N. Rochat,* Cea, Leti, Minatec, France*; L. Vallier, G. Cunge, O. Joubert,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

The complexification of 3D architectures of advanced CMOS devices require to etch materials with a sub-nanometer accuracy without introducing damage to the surface and with infinite selectivity between the materials in presence. The Smart etch concept is a n original etching approach which has successfully been proposed to etch silicon nitride spacer with less than 1nm of spacer dimension loss and SiGe recess. This technic relies on a surface modification by H or He ion implantation performed in capacitive coupled plasma (CCP) reactor, followed by a selective removal of the modified layer over the pristine material. The selective removal can be achieved either by wet or remote plasma source etching. Today, the mechanisms driven the etch selectivity between the pristine and modified SiN layers in remote plasma are still misunderstood

In this paper, we propose to investigate the etching mechanisms of pristine and implanted silicon nitride layers in NH_3 /NF_3 remote plasma. The etching experiments are performed in 300mm industrial prototype of reactor, equipped with both a CCP and a remote plasma source allowing to achieve the implantation and the removal steps in the same reactor chamber. The substrate temperature can be varied from 40 to 200°C during the process. The etching kinetics are followed in real time thanks to in situ kinetic ellipsometry. The SiN layers are characterized by XPS, XRR and Tof-SIMS.

The real time monitoring of the etching reveals that there is a delay before the SiN layers are etched for any plasma conditions and wafer temperature. The incubation time increases with substrate temperature and depends on the surface state. For instance, our results show that a deoxidized SiN surface using HF wet is not etched in NH_3/NF_3 remote plasma, proving that the oxygen acts as a catalysis of the reaction, and subsequent material etching. Moreover, it is shown that the main impact of the He or H_2 implantation step is to functionalize the SiN surface by implanting residual oxygen present in the chamber and generating dangling bond. Thus, the incubation time when etching implanted SiN layers in NH_3/NF_3 plasma at 100°C is only of 30s compared to 84s for pristine SiN. This means that short duration of remote plasma is the key parameter to achieve, infinite selectivity between implanted and pristine SiN surface.

Thin Films Division
Room 102A - Session TF+AS+EL+PS-ThM
In-situ Characterization and Modeling of Thin Film Processes

Moderator: Thomas Riedl, University of Wuppertal

8:00am **TF+AS+EL+PS-ThM1 Defects in Thin Films: A First Principles Perspective**, ***Douglas Irving,*** *J.S. Harris, J.N. Baker, S. Washiyama, M.H. Breckenridge,* North Carolina State University*; P. Reddy,* Adroit Materials*; R. Collazo, Z. Sitar,* North Carolina State University **INVITED**

Realization of next-generation power and optoelectronic devices depends on the ability to controllably donor dope thin films of AlN and Al-rich AlGaN. The challenge in donor doping these materials begins with the donor dopant itself, Silicon. While it is a common shallow donor dopant in GaN, it exhibits a deeper ionization level in AlN due to the formation of a DX center near the conduction band minimum. Compensation in both the low and the high doping regime also presents a significant technical challenge to the doping of AlN thin films. In this talk, we explore the mechanisms for compensation in Si-doped AlN in the low and high doping regimes. For this purpose, we have implemented first principles density

functional theory calculations with screened hybrid exchange-correlation functionals to determine the properties of individual defects in AlN. The formation energies of each defect are used within a grand canonical equilibrium model to identify the predominant defects as a function of growth conditions. In the low doing regime, important to drift layers in power electronics, we find unintentional impurities and unintentional impurity complexes are often responsible for free carrier compensation. Compensation in films that are doped to higher impurity concentration is found to be related to vacancy-dopant complexes. Possible solutions unique to thin films have also been explored and will be presented. Results from these methods are compared with complementary experimental data that includes below band gap optical absorption and photoluminescence, electrical measurements, dopant implantation, and available SIMS measurements.

8:40am **TF+AS+EL+PS-ThM3 Advances in Numerical Simulation of SiN ALD*,* *Paul Moroz,*** TEL Technology Center, America, LLC

Atomic layer deposition (ALD) includes a fast growing area of applications and could be foreseen as becoming one of the leading semiconductor technologies. In many cases, it allows accurate atomic-scale deposition of films with almost conformal profiles. Here we present new results on the Monte Carlo feature-scale simulations of ALD conducted with a feature-profile simulator, FPS3D [1-5], as well as comparison of obtained simulation results with the corresponding experiments. The ALD processes are often complex, involving large molecules and, to our knowledge, have not been addressed by other feature-profile simulations except FPS3D. The main factor of all of ALD schemes is the cyclic change in flux parameters and in the corresponding surface chemistry, which results in a single monolayer or, most typically, in a fraction of a monolayer of a film deposited after application of a cycle. Here, we consider a case of ALD with two time-steps: (1) dichlorosilane gas and (2) ammonia plasma. The SiN deposition rate in this case is about a half of a monolayer per cycle. A set of surface reactions is considered which emphasize the steric hindrance effect that was found to be an important factor in explaining deposition rates for this ALD process.

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[4] P. Moroz, 15th Int. Conf. on Atomic Layer Deposition, Portland, OR (2015).

[5] P. Moroz, D. J. Moroz, Japan. J. Appl. Phys. **56**, 06HE07 (2017).

9:00am **TF+AS+EL+PS-ThM4 Diffusion Kinetics Study of Adatom Islands: Activation Energy Barriers Predicted using Data-driven Approaches*,* *ShreeRam Acharya,*** *T.S. Rahman,* University of Central Florida

The Self-Learning Kinetic Monte Carlo (SLKMC) method [1] with a pattern recognition [2] and a diffusion path finder scheme enables collection of a large database of diffusion processes including single- and multiple-atoms, and concerted island motion and their energetics. The databases collected from adatom-island (2-8 atoms) diffusion characteristics for a large set of homo- and hetero-epitaxial metallic systems (Cu, Ni, Pd and Ag) are used to extract a set of easily accessible features, geometrical and energetic, using physical insight which are then encoded. Those features along with activation energy barrier are used to train and test linear and non-linear statistical models. A non-linear model developed based on neural network technique predicts the diffusion energy barriers with high correlation with the calculated ones. In this talk, we present the results of kinetics study of these homo or hetero-epitaxial metallic systems some of whose barriers are used for training of the model and are compared to the corresponding quantities obtained from KMC simulation using energy barriers calculated from computationally intensive interatomic interaction potential based approach.

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Work supported in part by MMN-1710306.

9:20am **TF+AS+EL+PS-ThM5 Using Ellipsometry and XPS to Understand the Degradation of Thin-film Aluminum Mirrors Protected by Ultrathin Fluorides*,*** *M.R. Linford,* ***Brian I. Johnson****,* *R.S. Turley, D.D. Allred,* Brigham Young University

The LUVOIR (Large, UV-optical-IR) telescope is a potential NASA flagship space-based observatory of the 2020's or 30's. It will utilize the largest mirrors ever put into space. The reflective coating for the mirrors will be aluminum, since there is no material with comparable reflectance at shorter wavelengths. However, to achieve high reflectance over the broadest energy range, the top surfaces of such Al mirrors must be protected against the formation of oxide layers that form quickly in air using wide-bandgap fluoride coatings, traditionally about 25 nm of MgF_2. Researchers have been endeavoring to use fluorides which are transparent further into the VUV (vacuum ultraviolet) like LiF and AlF_3, and to make these barriers more continuous by depositing them on heated surfaces and making the barriers thinner. However, when the barriers are thinner and when materials like LiF are exposed to moist air, degradation of VUV reflectance is observed. Thus, studying fluoride barrier-coated mirrors is vital. We have recently reported on the time dependent growth of apparent aluminum oxide thickness for two Al mirrors protected by ultrathin fluoride layers. These measurements were based on variable-angle, spectroscopic ellipsometric (VASE) measurements. (Allred, Thomas, Willett, Greenburg, & Perry, 2017) (Miles, 2017) . VASE, however, does not provide chemical composition data. An independent analytical technique which is sensitive to surface composition is required. We have undertaken such investigations using X-ray photoelectron spectroscopy (XPS), and now report on correlations between optical properties and XPS for fluoride-coated aluminum mirror test structures.

9:40am **TF+AS+EL+PS-ThM6 Model for Amorphous Thin Film Formation and Validation*,* *Rahul Basu,*** VTU, India

A coupled set of equations describing heat and mass transfer during phase transformation is formulated The model is extended to incorporate surface convective effects. These equations which are non linear due to the moving interface are linearized and decoupled. Effects of various heat transfer parameters are analyzed through small parameter expansions. Solutions obtained via this artifice allow closer examination of surface effects on the boundary layer of the phase transformation. A relation is found for the effect of the glass transition temperature versus the boundary layer thickness for several alloys in various groups of the Periodic Table. Earlier work and results are analyzed in light of the present analysis.

11:00am **TF+AS+EL+PS-ThM10 2D TMD Monolayer of MoS_2 BY ALD and Insight in the Mechanism by Surface Organometallic Chemistry*,* *Elsje Alessandra Quadrelli,*** CNRS CPE Lyon, France **INVITED**

Atomically-thin crystalline domains of MoS_2 [1] or WS_2 [2] are obtained from an organometallic amorphous deposit obtained by ALD/MLD.

This original result with respect to the state of the art has been mechanistically rationalized with in situ and in operando modelling studies on the oxide nanobeads at different annealing temperatures. This contribution will present the surface organometallic method, the characterization of the 2D layers (among which the first in-plane micrographs of ALD-grown MoS_2 samples)[1] and the proposed surface coordination chemistry mechanism at hand obtained with model studied on 3D silica beads. These model studies couple in operando infra-red spectroscopy, gas-chromatography detection of the released by-products and atomic composition of the deposit at each cycle, leading to molecular level understanding of the growth process.

***Acknowledgments** : This work was carried out within the framework of the partnership between the C2P2 research unit (UMR 5265 CNRS CPE Lyon University Claude Bernard Lyon 1) and CEA's Directorate of Technological Research (DRT) on the nanochemistry platform installed in CPE Lyon. The authors of the papers below thank CPE Lyon, CNRS, CEA / LETI (Silicon Technology Department and nanocharacterization platform) for the support and the DRF / INAC for the collaboration in the framework of the "2D Factory" project.*

***Ref** : [1] Cadot et al.Nanoscale , **2017**, 9, 467. [2] Cadot et al. JSVT A **2017**, 35, 061502 .*

11:40am **TF+AS+EL+PS-ThM12 A Novel Fourier Transform Ion Trap Mass Spectrometer for Semiconductor Processes*,* *Gennady Fedosenko,*** *H.-Y. Chung, R. Reuter, A. Laue, V. Derpmann, L. Gorkhover, M. Aliman, M. Antoni,* Carl Zeiss SMT GmbH, Germany

Real-time inline control of process gas compositions with high sensitivity has been of particular importance in recent years in the semiconductor industry and beyond. Commonly quadrupole residual gas analyzers (RGA) are used, together with Optical Emission Spectroscopy (OES) for process control and process development. However, most RGAs are not capable of measuring a whole mass spectrum fast enough to monitor etch or deposition processes of a few seconds. A new process control mass

spectrometer, based on Fourier-Transform 3D Quadrupole Ion Trap technology, is more appropriate for real-time inline process monitoring.

The 3D-Quadrupole Ion Trap mass spectrometer *iTrap*® by ZEISS is installed in a vacuum chamber (~ 120mm x 120mm x 500mm) with a fast switching valve for pulsed gas sample injection (pulse duration ~ 50ms or less). An electron gun is used for ionization of the gas pules. The Ion Trap achieves ion trapping and accumulation by means of a radio frequency applied to the ring electrode of the trap. With the aid of advanced electronic amplifiers and selective ion excitation technique the ion oscillations can be measured electrically by means of the induced current on the cap electrodes without using any separate particle detector. The mass spectrum can be finally obtained in less than one second.

Real-time measurements of the hydrogen plasma cleaning process of Sn contaminated samples were performed with the *iTrap* mass spectrometer. The working pressure of the plasma cleaning process was 0.5 mbar. Decreasing signal of SnH_4 and other contaminations from the samples which are directly correlated to the cleaning process were observed with *iTrap*. This result is extremely useful for the process control of plasma processes and inline real-time contaminations control for high-end applications.

Inline measurement at a MOCVD chamber showed that *iTrap* is capable to detect reaction products, contaminations on the wafer holder and dopant memory in real-time. These results demonstrate that *iTrap* is a very sensitive and fast process mass spectrometer suitable for real-time inline process monitoring.

Many etch processes take place in 10 to 30 s process steps. Different processes were examined with e.g. HBr or BCl_3 chemistry together with several wafer materials such as Silicon, Hafnium Oxide or Titanium Nitride. The obtained mass spectra show the etch plasma chemistry together with etch reaction products (HfClx, SiClx, etc.). This data gives new insight into the etch processes, which until now were rarely understood on a chemical level. First wafer effects related to the chamber cleaning and pre-coating steps prior to the etch step were also examined.

12:00pm **TF+AS+EL+PS-ThM13 Realization of Shifts in Threshold Voltage and Subthreshold Swing in Atomic Layer Deposited Zinc Oxide As Channel Layer through *in-situ* Half-Cycle Analysis**, ***Harrison Sejoon Kim**, A.T. Lucero, S.J. Kim, J. Kim,* University of Texas at Dallas

Thin film process monitoring of atomic layer deposition (ALD) has been adopted as the versatile technique to identify both chemical and physical properties of ALD films. Their *in-situ* characterization technique includes mostly Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and quartz crystal microbalance analysis. [1–3] However, currently there are no reports on monitoring the results of sub-nm device physics even if we are already in the era of beyond 10 nm node semiconductor processes. Moreover, even if there are a few initial studies, demonstrating *in-situ* electrical characterization with ALD, it requires device packaging, which ultimately limits the flexibility to be further characterized. [4]

In this current work, we have developed an ultra-high vacuum (UHV) cluster tool equipped with thermal processing, plasma surface treatment, thin film deposition, and electrical characterization which can be performed *in-situ* (Figure 1). With this feasibility, we demonstrate the deposition of semiconducting zinc oxide (ZnO) in inverted-coplanar structured thin film transistors (TFT). Diethylzinc (DEZ) and water (H_2O) is used as ALD precursors at 100°C. DEZ and H_2O half-cycle analysis is carried out to monitor the interface states of ZnO/dielectric (Figure 2). Initially, 45 ALD cycles of ZnO have shown switching behavior with an on/off ratio of ~10^2 in vacuum. Subsequent ALD cycle shifts the threshold voltage (V_{th}). V_{th} shifts associated with each ALD cycle are assumed to be attributed to the changes in interface trap density as a result of interface state passivation in ZnO during its growth, especially passivating fixed oxide charges (Q_{ox}). To understand interface states of ZnO and the bulk of oxide better, further analysis of shift of subthreshold swing (SS) is demonstrated. Since shifts in SS best represents changes in interface trap density, [5] it is worthwhile to note the changes in SS in metal-oxide-semiconductor transistors.

This work was supported by the Creative Materials Discovery Program on Creative Multilevel Research Center (2015M3D1A1068061) through the National Research Foundation(NRF) of Korea funded by the Ministry of Science, ICT & Future Planning.

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Thin Films Division
Room 104B - Session TF+PS-ThM
Deposition Processes for 3D and Extreme Geometries

Moderators: Richard Vanfleet, Brigham Young University, AnnaMaria Coclite, Graz University of Technology

8:00am **TF+PS-ThM1 ALD and Diffusion in High Aspect Ratio Carbon Nanotube Forests**, ***David Kane**, R.C. Davis, R.R. Vanfleet,* Brigham Young University

Very high aspect ratio or nanostructured materials have numerous applications. In many of those applications, the surface is decorated by atomic layer deposition or other vapor phase deposition techniques. In these extreme geometries the uniformity of deposition is a function of the interplay between transport (diffusion) and reaction rates. The A-B cycling in Atomic Layer Deposition (ALD) separates the deposition reaction from the transport. We have observed a limited penetration depth which decreases with cycle number in ALD on vertically aligned multiwall carbon nanotube (MWCNT) forests with an effective aspect ratio of 1000. Models of ALD in high aspect ratio features based on Knudsen diffusion transport combined with a simple geometric model of nucleation and growth on surfaces with a low nucleation site density can qualitatively reproduce the observed deposition. Fitting the models to the data allows extraction of the diffusion coefficients for these confined geometries.

8:20am **TF+PS-ThM2 Nanoporous Reference Substrates for ALD on High Aspect Ratio High Surface Area Materials**, ***Dmitri Routkevitch**,* InRedox

Deposition of conformal and uniform coatings onto high aspect ratio high surface area substrates and materials is a unique domain of ALD impacting many important applications, including energy generation and storage, semiconductor device manufacturing, chemical and biosensing and many others. However, ALD process development on such substrates is hindered by complex material geometry leading to poorly understood transport conditions and high cost of real substrates, such as large Si wafers at later staged of processing. In addition, modern ALD reactors, designed and optimized for high speed processing of flat substrates, require validation of uniformity and conformality of ALD coatings both inside the pores and laterally across the high surface area substrates with complex multiscale topology.

Nanoporous Anodic Aluminum Oxide (AAO) – a self-organized material resembling nanoscale honeycomb – is a controllable, well-defined, inexpensive and convenient nanomaterial platform to support the development and validation of high surface area ALD. The combination of ALD with AAO enables control of both the nanoscale geometry and chemistry with unprecedented precision to provide new avenues for design and engineering of functional materials and devices.

Some of the benefits of AAO as a reference ALD substrate are:

1. Highly uniform and parallel cylindrical pores, complex pore structures (modulated, branched, etc) available to emulate different pore size distributions of other materials.
2. A broad spectrum of transport conditions (pore diameters from 2 nm to 500 nm and pore lengths from <100 nm to >300 µm for aspect ratio (L/D) from 1 to as high as 50,000) that could be tested to aid better understanding and rapid development of new ALD processes.
3. Reproducible and well-understood surface chemistry of alumina makes it nearly universally suitable for many binary reactions involved in ALD.
4. High pore densities (10^{12} to 10^7 cm^{-2}) allow straightforward characterization of elemental depth profiles by EDS even for very thin (5-10 nm) coatings.
5. Available in different form factors and on different substrates (flexible foils and tapes, rigid plates, Si wafers, glass blanks, etc) to accommodate different types of ALD reactors, such reel-to-reel reactors for coating battery electrodes or reactors designed to process stacks of Si wafers or PV substrates.

Scaleable to large sizes, low cost.

Several case studies will be presented where AAO was used as a reference substrate to aid the development of ALD for high surface area materials.

8:40am **TF+PS-ThM3 Fine-tuned Resistive Coatings for Detector Applications**, ***Maximilian Gebhard**, A.U. Mane, D. Choudhury, S. Letourneau, D.J. Mandia, Y. Zhang, J.W. Elam,* Argonne National Laboratory

An important building block for detector devices are amplifiers, such as microchannel plates (MCPs). Due to the geometry of several periodically arranged microchannels, incident electrons or irradiation can be amplified by several orders of magnitude, making MCPs highly efficient in several applications such as neutron detectors and night-goggles. The efficiency of state-of-the-art MCPs is strongly related to functional coatings, acting as resistive coating and secondary electron emission (SEE) layer. While the SEE material (*e.g.* Al_2O_3 or MgO) should exhibit a high SEE coefficient, the resistive coating must facilitate a uniform and stable electrostatic field along the pores and during operation. It was shown previously that atomic layer deposition (ALD) is capable to produce highly efficient SEE coatings (MgO) as well as a fine-tuned resistive coating directly on the MCP substrate, thereby improving the overall performance of the detector devices.[1,2] By producing highly conformal thin films over large areas and on large aspect ratios, ALD is the method of choice to produce functionalized MCPs.

One challenge in manufacturing reliable MCPs for advanced applications are external conditions like ambient temperature. With temperature gradients of 100 K or higher, the thermal coefficient of resistance (TCR) of the resistive coating plays a major role with respect to electrical transport phenomena. Positive TCRs can cause increased resistance at elevated temperatures and in due turn a collapse of the MCP's performance. Similar determining factors are on hand for strongly decreased temperatures. A second challenge is the fluorine-based chemistry, which is currently often employed to produce ALD-functionalized MCP coatings.

We present here the development of ALD-fabricated materials, being free of fluorine chemistry and exhibiting tailored electric resistance over a broad temperature range as well as promising performance as resistive coating in MCPs. Apart from thorough process development, those transition metal-based materials were analyzed regarding their composition, structure and electrical behavior employing XPS, SEM, XRD and extended IV-measurements. Furthermore, the coatings were applied to MCPs, which were tested for their performance.

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9:00am **TF+PS-ThM4 Tungsten Atomic Layer Deposition on Vertically Aligned Carbon Nanotube Structures**, ***Ryan Vanfleet**, R.C. Davis, D.D. Allred, R.R. Vanfleet,* Brigham Young University

Carbon Nanotubes (CNTs) can be grown from 2D patterns into high aspect ratio, 3D MEMS structures. These porous structures can then be filled solid with different materials in order to impart specific and unique properties to the MEMS device. Tungsten, with its conductivity, high density and high temperature resistance, could be of special interest for many MEMs devices. Due to the high packing density and high aspect ratios of vertically aligned CNT forests, it is difficult to uniformly deposit films throughout the entirety of the structure. Atomic Layer Deposition (ALD) has been shown to uniformly coat structures with extreme geometries using sequential, self-limiting surface reactions. This in an inherently slow process, especially on geometries where the deposition is diffusion-limited such as in CNT forests. Approximately 50 nm of tungsten is required to fill a CNT-patterned structure solid where the individual CNTs grow roughly 100 nm apart. The tungsten ALD process has been shown to be able to deposit more than a single atomic layer per cycle so that the necessary number of cycles to fill the CNT structure is reduced. The process parameters that facilitate this increased deposition rate will be discussed. Tungsten-filled CNT beams were subjected to three-point bending tests to determine material properties of the composite structures. Preliminary tests on beams with about 35 nm of as-deposited tungsten give an ultimate strength of 11 MPa and a Young's Modulus of 1.7 GPa. The microstructure of the as-deposited tungsten is extremely fine and annealing studies will also be addressed.

9:20am **TF+PS-ThM5 ALD in Metal Organic Frameworks: Toward Single Site Synthesis and Sinter-Resistant Catalysts**, ***Alex Martinson**,* Argonne National Laboratory **INVITED**

Reproducibly and homogeneously synthesizing single-site transition metal catalysts on exceedingly high surface area supports with stability under catalytic conditions remains a grand challenge. To address this challenge, we utilize atomic layer deposition (ALD) in metal-organic frameworks (MOFs), a process we call AIM. Here, ALD provides a straightforward gas phase route to access a wide variety of small precision clusters with spatial and dimensional homogeneity. The well-defined structure of MOF NU-1000 framework and nodes allows for detailed characterization of their size and uniforming as well as insight into their inherent stability. This talk will discuss several classes of ALD precursors and processing conditions that have been identified to be compatible with few-atom cluster deposition in Zr-based MOF NU-1000.

11:00am **TF+PS-ThM10 Alumina Deposition by Atomic Layer Deposition (ALD) on Flat Surfaces and High Aspect Ratio Structures**, ***Dhruv Shah**, D.I. Patel, D.J. Jacobsen, J.E. Erickson, M.R. Linford,* Brigham Young University

Atomic layer deposition (ALD) involves layer-by-layer deposition due to sequential exposure of two precursors to as substrate . ALD was developed in the late 1970s by Suntola and co-workers as a modification of chemical vapor deposition (CVD). In ALD, the dosing and purging steps are separated to ensure that each precursor saturates the surface before the other precursor enters the chemical reactor. ALD is widely used in the semiconductor and microelectronics industry to deposit thin films of various oxides on different substrates. ALD can be operated in two modes: plasma assisted and thermally assisted. Thermally assisted ALD has been widely used due to its high uniformity and conformality in depositing thin films on a variety of substrates.

Here we report alumina deposition by ALD using trimethylaluminum and water as precursors on silicon substrates. We optimized the process on flat surfaces like silicon shards, and extrapolate the process to high aspect ratio devices and powders, ultimately confirming the deposition on these high aspect ratio materials. Achieving high degrees of consistency and uniformity for deposition on powders through a frit using ALD has been difficult. We tried multiple recipes for alumina deposition, optimizing the dose time, purge time and effective exposure of the precursor on the substrate to achieve uniform results. Our thin films are characterized by spectroscopic ellipsometry (SE), water contact angle goniometry, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and/or transmission electron microscopy (TEM). The thin films we have obtained on planar substrates using ALD vary in thickness from 0.5 – 41.0 nm. These thin films were used to conduct a multiple sample analysis (MSA) in SE to obtain the optical constants of alumina. Since alumina is one of the most commonly used material in microfabrication, its optical constants will be useful in the field.

11:20am **TF+PS-ThM11 Resistivity of the Alumina Diffusion Barrier in Catalytic Carbon Nanotube Growth**, ***Berg Dodson**, G. Chen, R.C. Davis, R.R. Vanfleet,* Brigham Young University

By using photolithography techniques and catalytically grown carbon nanotubes (CNTs) it is possible to fabricate high aspect ratio structures that can be used as scaffolds for MEMS devices. The drawback of making CNT structures this way is it is difficult to electrically connect to them since they are grown on an insulating alumina layer. However, previous work demonstrates that the alumina layer becomes conductive during CNT growth. Two-point probe measurements from tungsten to a CNT post in a 100 nm tungsten/alumina 50 nm/CNT stack yielded 580 ± 65 Ω. I present TEM based data showing how this change in conductivity correlates with iron and carbon diffusing into the alumina layer during CNT growth. I will also show how the observed diffusion in these samples compares with what is predicted by diffusion models as well as how the change in resistivity compares to what is expected in doped alumina.

11:40am **TF+PS-ThM12 High Temperature Active CeO_2 Nanorods Generated via Diffusion Limited Atomic Layer Deposition**, ***Haoming Yan**, X.Z. Yu, Q. Peng,* University of Alabama

CeO_2 has attracted lots of attention due to its superior oxygen storage and donating ability as a catalyst support. CeO_2 nanorods has the best donating ability than all the other types of CeO_2 materials. However, the nanorods change its morphology and lose its activity at 400°C or above. Therefore, improving the thermal stability of CeO_2 nanorods can unlock the potential applications of CeO_2 nanorods in the high temperature applications. In this work, we introduce a diffusion-limited Al_2O_3 atomic layer deposition to

selectively passivate the surface site of CeO_2 nanorods, largely enhancing its thermal stability and its oxygen storage capacity simultaneously.

Electronic Materials and Photonics Division
Room 101A - Session EM+2D+NS+PS+RM+TF-ThA

IoT Session: Flexible Electronics & Flash Networking Session

Moderators: Shalini Gupta, Northrop Grumman ES, Sang M. Han, University of New Mexico

2:20pm **EM+2D+NS+PS+RM+TF-ThA1 Epitaxial Electrodeposition of Electronic and Photonic Materials onto Wafer-size Single Crystal Gold Foils for Flexible Electronics***, **Jay Switzer,*** Missouri University of Science and Technology **INVITED**

Single-crystal silicon (Si) is the bedrock of semiconductor devices due to the high crystalline perfection that minimizes electron-hole recombination, and the dense SiO_x native oxide that minimizes surface states. There is interest in moving beyond the planar structure of conventional Si-based chips to produce flexible electronic devices such as wearable solar cells, sensors, and flexible displays. Most flexible electronic devices are based on polycrystalline materials that can have compromised performance due to electron-hole recombination at grain boundaries. In order to expand the palette of electronic materials beyond planar Si, there is a need for both an inexpensive substrate material for epitaxial growth, and an inexpensive and scalable processing method to produce epitaxial, grain-boundary-free films of metals, semiconductors, and optical materials. Recently, in our laboratory, we have developed a process for producing wafer-size, flexible, and transparent single-crystal Au foils by an electrochemical processing method.[1] Au is epitaxially electrodeposited onto Si using a very negative applied potential. An interfacial layer of SiO_x is then produced photoelectrochemically by lateral undergrowth. The Au foil is then removed by epitaxial lift-off following an HF etch. We will report on the electrodeposition of epitaxial films of metal oxide semiconductors such as Cu_2O and ZnO onto the highly-ordered and flexible Au foils. We will also present new, unpublished results in which we spin-coat epitaxial films of perovskites, such as $CsPbBr_3$, directly onto these Au foils and onto other single crystals.

Acknowledgement: This presentation is based on work supported by the U.S. Department of Energy, Office of Basic Sciences, Division of Materials Science and Engineering under grant No. DE-FG02-08ER46518.

[1] Mahenderkar N., Chen Q., Liu Y.-C., Duchild, A., Hofheins, S. Chason E., Switzer J (2017). Epitaxial lift-off of electrodeposited single-crystal gold foils for flexible electronics. Science, **355**, 1203-1206.

3:00pm **EM+2D+NS+PS+RM+TF-ThA3 Flexible Electronic Devices Based on Two Dimensional Materials***, R. Kim, N.R. Glavin,* Air Force Research Laboratory*; R.H. Rai, K. Gliebe, M. Beebe,* University of Dayton; Air Force Research Laboratory*; J. Leem, S. Nam,* University of Illinois at Urbana-Champaign*; R. Rao,* Air Force Research Laboratory*; **Christopher Muratore,*** University of Dayton*; K.M. Burzynski,* University of Dayton and Air Force Research Laboratory, Materials and Manufacturing Directorate

Low temperature synthesis of high quality 2D materials directly on flexible substrates remains a fundamental limitation towards realization of robust, strainable electronics possessing the unique physical properties of atomically thin structures. Here, we describe room temperature sputtering of uniform, stoichiometric amorphous MoS_2, WSe_2, and other transition metal dichalcogenides and subsequent large area (>2 cm^2) photonic crystallization to enable direct fabrication of two-dimensional material photodetectors on large area flexible PDMS substrates. Fundamentals of crystallization kinetics for different monolithic and heterostructured TMDs are examined to evaluate this new synthesis approach for affordable, wearable devices. The photodetectors demonstrate photocurrent magnitudes and response times comparable to those fabricated via CVD and exfoliated materials on rigid substrates and the performance is unaffected by strains exceeding 5%. Other devices and circuits fabricated from crystallized 2D TMDs deposited on large area flexible substrates are demonstrated.

3:20pm **EM+2D+NS+PS+RM+TF-ThA4 Contact Resistances and Schottky Barrier Heights of Metal-SnS Interfaces***, **Jenifer Hajzus,** L.M. Porter,* Carnegie Mellon University*; A. Biacchi, S. Le, C. Richter, A. Hight Walker,* National Institute of Standards and Technology (NIST)

Tin(II) sulfide (SnS) is a natively p-type, layered semiconductor that is of interest for two-dimensional and optoelectronic applications. Understanding the behavior of contacts to SnS is essential for its use in devices. In this work, contact metallizations with a range of work functions were characterized on both solution-synthesized, p-type SnS nanoribbons and electron-beam evaporated, polycrystalline SnS thin films. The structure and properties of electron-beam evaporated SnS films were dependent upon deposition temperature and post-deposition annealing. A deposition temperature of 300 °C followed by vacuum annealing at 300 °C resulted in p-type, orthorhombic SnS films. Specific contact resistances of Ti/Au, Ru/Au, Ni/Au, and Au contacts were measured on SnS films using circular transfer length method (CTLM) patterns prior to and after annealing the contacts at 350 ° C in argon. All metallizations on SnS thin films were ohmic prior to annealing. A trend of decreasing average specific contact resistance with increasing metal work function was observed for the as-deposited contacts. Annealed Ru/Au exhibited the lowest average specific contact resistance of ~1.9×10^{-3} Ω -cm^2. Contacts were additionally patterned onto individual, solution-synthesized SnS nanoribbons. In contrast to the behavior of contacts on electron-beam evaporated films, low work function metals (Cr/Au and Ti/Au) formed Schottky contacts on SnS nanoribbons, whereas higher work function metals (Ni/Au and Pd/Au) formed ohmic or semi-ohmic contacts. Ni/Au exhibited a lower contact resistance (~10^{-4} Ω cm^2 or lower) than Pd/Au (~10^{-3} Ω cm^2 or lower). Schottky barrier heights and ideality factors of Cr/Au and Ti/Au contacts were extracted by fitting current-voltage measurements to a back-to-back Schottky diode model. The ohmic behavior for Ni/Au and Pd/Au and the calculated Schottky barrier heights (0.39 and 0.50 eV for Cr/Au and Ti/Au, respectively) on SnS nanoribbons agree well with behavior predicted by Schottky–Mott theory and suggest a lack of Fermi level pinning.

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

Atomic Layer Processing: Integration of ALD and ALE

Moderator: Scott Walton, U.S. Naval Research Laboratory

2:20pm **PS+EM+TF-ThA1 Atomic-Layer Etching (ALE) of Nickel or Nickel Oxide Films by Hexafluoroacetylacetone (HFAC) Molecules***, **Abdulrahman Basher,** M. Isobe, T. Ito, K. Karahashi,* Osaka University, Japan*; M. Kiuchi,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; T. Takeuchi,* Nara Women's University, Japan*; S. Hamaguchi,* Osaka University, Japan

Atomic layer etching (ALE) is one of the most promising technologies and a prospective solution to various technical problems in nanometer-scale device fabrication processes. ALE consists of a series of processing cycles and, in each cycle, a transition step to form a reactive thin layer on the material surface is followed by a removal step to take off only this modified layer. For a metallic film, the formation of volatile organic metal complexes may be used to establish low-damage ALE processes. In this study, to explore the possibility of establishing new etching processes for the manufacturing of magnetoresistive random access memories (MRAMs), we examine possible etching reactions of magnetic materials with organic molecules. In this study, we select Ni as a sample of ferromagnetic materials. An earlier studies [1,2] indicated that hexafluoroacetylacetone (hfac) may be used for etching of Ni due to the possible formation of nickel(II) hexafluoroacetylacetonate $Ni(hfac)_2$. According to [2], if a Ni surface is oxidized and then exposed to gas-phase hfac, $Ni(hfac)_2$ are formed when the substrate temperature is increased. It is pointed out that, without the oxidation process, $Ni(hfac)_2$ is not formed under similar conditions. Therefore, the expected single cycle of Ni ALE by gas-phase hfac is as follows; a Ni surface is first exposed to oxygen and then to hfac. This step is then followed by the increase of substrate temperature. In this study, however, the goal of this study is to understand the interaction mechanisms between hfac and a Ni or NiO surface and we use the first principles calculation to examine the interaction of a hfac molecule with a Ni or NiO surface atoms. The simulation results based on Gaussian 09 that we have obtained so far suggest that the transfer of a proton from an enol hfac molecule to the Ni or NiO surface generates its deprotonated anion, whose oxygen atoms strongly interact with a positively charged Ni atom on the surface and thus form a precursor of a highly volatile metal complex. Difference in charge distribution between Ni and NiO surfaces affects the likelihood of the formation of such precursors. Surface roughness may also affect such surface reactions.

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[1] Chen J. K., Altieri N. D., Kim T., Chen E., Lill T., Shen M., and Chang J. P., " Direction etch of magnetic and noble metals. II. Organic chemical vapor etch," *J. Vacuum Sci. & Tech. A***35**, 05C305 (2017).

[2] Nigg H. L. and Masel R. I., " Surface reaction pathways of 1,1,1,5,5,5-hexafluoro-2,4-pentandione on clean and pre-oxidized Ni(110) surface," *J. Vacuum Sci. & Tech. A***17**, 3477 (1999)

2:40pm **PS+EM+TF-ThA2 Thermal Atomic Layer Etching of HfO_2 Using HF for Fluorination and $TiCl_4$ for Ligand-Exchange***, Y. Lee,* ***Steven George,*** University of Colorado at Boulder

Thermal atomic layer etching (ALE) can be accomplished using sequential fluorination and ligand-exchange reactions. HF has been a typical fluorination reactant. Various metal precursor s have been used for ligand-exchange such as $Sn(acac)_2$, $Al(CH_3)_3$ and $AlCl(CH_3)_2$ and $SiCl_4$. This study explored $TiCl_4$ as a new metal chloride precursor for ligand-exchange. Thermal HfO_2 ALE using $TiCl_4$ and HF as the reactants was studied using i*n situ* quartz crystal microbalance (QCM) measurements from 200 - 300 °C. The HfO_2 films were etched linearly versus number of $TiCl_4$ and HF reaction cycles. The sequential $TiCl_4$ and HF reactions were also self-limiting versus reactant exposure. The QCM studies observed a mass change per cycle (MCPC) of -10.2 ng/(cm^2 cycle) at 200 °C and -56.4 ng/(cm^2 cycle) at 300 °C. These MCPCs correspond to HfO_2 etch rates of 0.11 Å/cycle at 200 °C and 0.59 Å/cycle at 300 °C. To explore the selectivity of thermal ALE using $TiCl_4$ and HF as the reactants, spectroscopic ellipsometry (SE) measurements were also employed to survey the etching of various materials. The SE results revealed that HfO_2 and ZrO_2 were etched by $TiCl_4$ and HF. In contrast, Al_2O_3, SiO_2, Si_3N_4, and TiN were not etched by $TiCl_4$ and HF. QCM studies also revealed that $TiCl_4$ and HF were able to etch Ga_2O_3. The etching selectivity can be explained by the reaction thermochemistry and the stability and volatility of the possible etch products. Al_2O_3 can also serve as an etch stop for HfO_2 ALE.

3:00pm **PS+EM+TF-ThA3 Rapid thermal-cyclic Atomic Layer Etching of SiO_2 Using Infrared Annealing***,* ***Nobuya Miyoshi,*** Hitachi High-Technologies, Japan*; H. Kobayashi, K. Shinoda, M. Kurihara,* Hitachi, Japan*; K. Kawamura, K. Ookuma, Y. Kouzuma, M. Izawa,* Hitachi High-Technologies, Japan

Device structures are changing from planar-types to three-dimensional types, such as fin-type field-effect transistors and gate-all-around transistors, in order to reduce leakage current and power consumption. Furthermore, fabricating these devices requires both high selectivity and precise control of device dimensions below the 10 nm scale. Atomic layer etching (ALE), which involves the layer-by-layer removal of thin films, is expected to meet these requirements. In a conventional ALE process for SiO_2[1], HF and NH_3 molecules are exposed to the surface simultaneously. In this case, the etching amount per cycle is proportional to square root of the exposure time of HF and NH_3, indicating that the process is quasi-self-limiting (not self-limiting).

We have been investigating a thermal ALE of SiO_2 in which ammonium fluorosilicate-based surface modified layer is formed after exposure to HF and NH_3 gas, and removed by using infrared annealing. Etching depth of blanket SiO_2 samples were measured by using in-situ ellipsometry. We found that self-limiting formation of the modified layer was achieved with separate exposure of HF and NH_3 gas. In addition, we successfully demonstrated that this etching process was highly selective with respective to poly-Si and SiN. Comparison between experimental results and Langmuir adsorption model for dependence of etching rate on partial pressure of HF and NH_3 clarified that the SiO_2 surface during the gas exposure is in adsorption-desorption equilibrium.

In addition to HF/NH_3 gas chemistry, we developed an ALE process utilizing plasma to generate HF molecule in stead of using HF gas. This process consists of plasma discharge for HF exposure, evacuation of the residual gas, NH_3 exposure, and infrared annealing. In the plasma discharge, fluorine based gases, such as CF_4, NF_3, and SF_6 were diluted by H_2 gas. The etching rate of SiO_2 saturated at 2.8 nm/cycle in regard to the discharge time, which indicates self-limiting behavior of the modification step. In contrast, the etching rates of poly-Si and SiN were below the detection limit of in-situ ellipsometry, demonstrating that this etching process for SiO_2 is highly selective to poly-Si and SiN.

[1] H. Nishio, et al., J. Appl. Phys. **74**, 1345 (1993).

3:20pm **PS+EM+TF-ThA4 The Smoothing Effect in Atomic Layer Etching (ALE)***,* ***Keren Kanarik,*** *S. Tan, W. Yang, I.L. Berry, T.B. Lill, Y. Pan, R.A. Gottscho,* Lam Research Corporation

Since the 1970s, the semiconductor industry has fabricated electronic circuits using a pattern-transfer approach that is remarkably reminiscent of the etching artform used centuries ago. Only, now, the patterns are a million times smaller, and require etching to within a few atoms on features less than 40 atoms wide. The most advanced etching technique in production today is called atomic layer etching (ALE). To the extent that an ALE process behaves ideally – with high ALE synergy and self-limiting behavior – the primary benefit is improved uniformity across all length scales: at the surface, between different aspect ratios, and across the full wafer. The focus here will be on the atomic-scale topography of the surface left behind after etching.

The purpose in this presentation is to introduce a new ALE benefit – the smoothing effect. By this, we mean that, beyond maintaining surface topography, ALE can improve the surface smoothness (ref 1). We will show that the effect in directional ALE is pervasive across different material systems, including Si, C, Ta, and Ru. We will propose explanations for the ALE smoothing phenomenon, and identify possible applications for this effect both inside and outside the semiconductor industry.

Ref 1: Kanarik, Tan, and Gottscho*. J. Phys. Chem. Rev.* submitted April 1, 2018.

4:00pm **PS+EM+TF-ThA6 Prospects for Combining ALD and ALE in a Single Chamber***,* ***Mike Cooke,*** Oxford Instruments, UK **INVITED**

There are obvious similarities between the process cycles of atomic layer deposition (ALD) and atomic layer etching (ALE), so could one machine do both? It is already the case that plasma enhanced chemical vapour deposition (PECVD) tools also perform etching, for the purpose of chamber cleaning. Deposition can also be performed in a tool configured for plasma etching, whether accidentally by creating a plasma with net deposition of fluorocarbon polymer, or by deliberately introducing gases such as silane. However, the wafer is usually heated above ambient in the range 100C – 400C for deposition, in both parallel plate PECVD and when using a high density plasma, while the wafer is typically cooled for etching.

There are also clear overlaps between the hardware requirements for atomic layer deposition and thermal atomic layer etching. The overlaps are more restricted for plasma enhanced ALD and ALE, because both the wafer temperature range and the character of the plasma can differ. In ALD there are benefits from using a remote plasma, because the plasma primarily creates a flux of radicals, while in ALE the plasma delivers both radicals and an ion bombardment flux. However, there is potential for combining plasma ALD and ALE in a chamber with an RF biased table. Thermal ALE and plasma ALE can be combined if the wafer table has a wide temperature range, and the tool can deliver doses of low vapour pressure ALE precursors.

The motivation for combining processes is less clear outside the academic community. Researchers wanting to access both precision etching and deposition under tight constraints of space and budget may be attracted to it, but the combination of halogen chemistry for ALE and organometallic precursors for ALD may make it difficult to change quickly between etching and deposition.

Results from ALE and ALD are presented to explore the overlap, including recent work on ALE and ALD for III-V power devices.

4:40pm **PS+EM+TF-ThA8 Low Temperature Surface Preparation of GaN Substrates for Plasma Assisted-Atomic Layer Epitaxial Growth***,* ***Samantha G. Rosenberg,*** U.S. Naval Research Laboratory*; D.J. Pennachio,* University of California, Santa Barbara*; M. Munger,* SUNY Brockport*; C. Wagenbach,* Boston University*; V.R. Anderson,* U.S. Naval Research Laboratory*; S.D. Johnson,* U. S. Naval Research Laboratory*; N. Nepal, A.C. Kozen, J.M. Woodward,* U.S. Naval Research Laboratory*; Z.R. Robinson,* SUNY Brockport*; K.F. Ludwig,* Boston University*; C.J. Palmstrøm,* University of California, Santa Barbara*; C.R. Eddy, Jr.,* U. S. Naval Research Laboratory

We have previously shown that using our low temperature plasma-assisted atomic layer epitaxy (ALEp) method we can grow AlN and InN for various applications.[1-3] The materials we have grown using our ALEp method have shown good crystalline quality, but suffer from an incorporation of carbon. Theory has led us to believe that the substrate preparation plays a significant role in the remediation of carbon, as that surface becomes the interface for the growth of the III-N film. Therefore, using surface science techniques, we strive to develop not only a fundamental understanding of the ALEp growth process but also atomic layer processes that will result in the best preparation method for a pristine GaN starting surface for ALEp.

In-situ surface studies of *in-situ* and *ex-situ* GaN substrate preparation and InN ALEp growth were conducted to advance fundamental understanding of the ALEp process. We conduct *in-situ* grazing incidence small angle x-ray scattering (GISAXS) experiments at the Cornell High Energy Synchrotron Source to investigate growth surface morphological evolution during sample preparation including a gallium-flash-off atomic layer process (ALP) at varying temperatures and number of cycles. GISAXS information is

complemented with *in-vacuo* x-ray photoelectron spectroscopy, reflection high-energy electron diffraction, and *ex-situ* atomic force microscopy studies conducted at the Palmstrøm Lab at UCSB, where we consider different *ex-situ* sample preparation methods to produce the most suitable GaN surface for our ALP/ALEp-based approach. We have determined that a combination of UV/ozone exposure followed by an HF dip produces the cleanest and smoothest GaN surface. We have further determined with GISAXS that ALP-based gallium-flash-off experiments performed at higher temperatures (500°C) produce a smoother starting surface than lower temperatures. Additionally we have determined that we should only perform ~10 cycles of ALP gallium-flash-off instead of 30 as was empirically chosen previously. Due to the sensitivity of the GISAXS experiment, we are able to observe the effect of individual components of the ALP process cycle (pulse vs purge), leading us to insights on the underlying chemical process of the gallium-flash-off ALP. Combining these two results, *ex-situ* and *in-situ* cleaning preparation, should lead us to the best GaN starting surface to grow high quality crystalline InN films.

[1] N. Nepal, et al., Appl. Phys. Lett. 103, 082110 (2013)

[2] C. R. Eddy, Jr, et al., J. Vac. Sci. Technol. A 31(5), 058501 (2013)

[3] R. S. Pengelly, et al., IEEE Trans. Microwave Theory Tech. 60, 1764 (2012)

5:00pm **PS+EM+TF-ThA9 Chemical Interactions with Alkali Compounds for Controlling the Transition between Thermal HF-based Atomic Layer Etching and Deposition*, John Hennessy,*** Jet Propulsion Laboratory, California Institute of Technology

The use of anhydrous hydrogen fluoride (HF) as a precursor can result in a variety of atomic layer deposition (ALD) processes for thin films like MgF_2, AlF_3 and LiF, with good optical properties in the deep ultraviolet. Cyclic exposure to HF and several organoaluminum compounds including trimethylaluminum (TMA), can also result in the thermal atomic layer etching (ALE) of some oxide films like Al_2O_3. In this work we show that the introduction of alkali halide compounds (such as LiF or KBr) into the reactor during this cyclic exposure can dramatically alter the deposition and etch conditions at a given substrate temperature. This occurs via the formation of an intermediate complex between the metalorganic precursor and the alkali compounds, that then enhances the removal of the surface fluoride created during the preceding HF exposure. Although the etch rate can be enhanced via this interaction at a given substrate temperature, the process remains self-limiting overall.

This approach provides a pathway to the low temperature (~100 °C) thermal ALE of Al_2O_3. This can be useful for substrate-sensitive applications where exposure to high temperature or energetic plasmas is undesirable. The interaction of TMA and the alkali halide also results in approaches for the spatially-selective deposition of AlF_3, or the spatially-selective etching of Al_2O_3.

We have utilized this combination of ALE and ALD to gently remove the native oxide from metallic aluminum and replace it with AlF_3 for a variety of optics and sensing applications at JPL. This can be performed by variation of the substrate temperature to switch continuously from ALE-mode to ALD-mode, or by variation of the aluminum precursor to tune the chemical interactivity with the alkali compounds. Fabricated devices made with this concept are relevant for a variety of NASA astrophysics and planetary science applications at ultraviolet wavelengths.

5:20pm **PS+EM+TF-ThA10 Selective Processing to Enable High Fidelity Control for the 5 nm Node*, Benjamen Rathsack,*** Tokyo Electron America, Inc.*; A. Ranjan,* TEL Technology Center, America, LLC.*; P.L.G. Ventzek,* Tokyo Electron America, Inc.*; H. Mochiki,* Tokyo Electron Miyagi, Ltd., Japan*; J. Bannister,* Tokyo Electron America, Inc. **INVITED**

Selective processing through the integration of Etch and ALD is critical to enable high fidelity control for 5 nm node structures. The complexity of multi-step integrations and processes has caused edge placement error (EPE) to become a critical challenge. The enablement of further scaling requires the utilization of self-aligned processing to address overlay variation as well as highly selective processing to address localized fidelity control. Fidelity control has become complex on multi-step processes integrated for SAQP, self-aligned block (multi-color) and high-aspect ratio structures. Localized fidelity control is highly dependent on both the material stacks and selective processing capabilities. This includes stringent selectivity, profile, loading and uniformity requirements. To meet these requirements, the fusion of Etch and ALD enables atomic level precision with minimal impact from CD loading effects. The fusion of Etch and ALD processing also improves across wafer CD control and LWR. The use of selective processing is demonstrated to be a key enabler of 5 nm node fidelity control.

Surface Science Division
Room 102A - Session SS+EM+PS+TF-ThA

Deposition, Etching and Growth at Surfaces

Moderator: Bruce E. Koel, Princeton University

2:20pm **SS+EM+PS+TF-ThA1 Controlled Deposition and High-Resolution Analysis of Functional Macromolecules in Ultrahigh Vacuum*, Giovanni Costantini,*** University of Warwick, UK **INVITED**

The ultimate spatial resolution of scanning tunnelling microscopy (STM) has allowed to gain an exceptional insight into the structure and the intra- and inter-molecular bonding of a huge number of adsorbed molecular system. Unfortunately, these remarkable analytical capabilities are achieved only under ultrahigh vacuum (UHV) conditions and therefore cannot be directly applied to more interesting systems composed of functional (bio)molecules or complex synthetic compounds. In fact, thermal sublimation is the strategy of choice for preparing ultrathin films of small and heat-resistant molecules in UHV but larger, complex (bio)molecules are not compatible with this process.

This challenge has been overcome in recent years by adapting soft-ionisation techniques developed in mass spectrometry (mainly electrospray ionisation, ESI) to transfer intact fragile molecules into the gas phase and to soft-land them onto atomically flat and clean substrates. When combined with advanced scanning probe microscopes operating under UHV conditions, these novel set-ups allow the surface deposition and high-resolution characterisation of a wide range of functional organic molecules and inorganic nanoparticles.

This talk will present recent advances in the development of ESI-deposition techniques and their combination with UHV-STM to analyse complex (bio)molecule-surface systems. It will start by reviewing the limits that standard molecular deposition imposes on the size of (bio)molecules that can by studied in surface science. It will continue by presenting a recently developed ESI-deposition setup based on a simple, efficient and modular design with a high intensity and mass selectivity. The discussion will then proceed to the application of ESI-STM to the characterisation of adsorbed polypeptides and polymers. In particular, it will be shown that this technique allows the imaging of individual macromolecules with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

3:00pm **SS+EM+PS+TF-ThA3 Unconventional Nucleation and Growth Kinetics: *in situ* Variable-temperature Scanning Tunneling Microscopy Studies of Chemical Vapor Deposition of Inorganic Monolayers on Metallic Substrates*, Pedro Arias,*** University of California, Los Angeles*; A. Abdulslam,* Colorado School of Mines*; A. Ebnonnasir,* University of California at Los Angeles*; C.V. Ciobanu,* Colorado School of Mines*; S. Kodambaka,* University of California, Los Angeles

The growth of thin films from atoms and/or molecules deposited from the gas phase onto solid substrates is a non-equilibrium phenomenon where the structure, composition, and crystallinity of the films are determined by kinetic and thermodynamic processes. Over the past few decades, vast and fruitful efforts have been devoted to understanding the kinetics of thin film growth. As a result, conventions of the kinetic factors have been developed to predict the growth mechanism and, hence, microstructure of the as-grown films: for example, nucleation at terraces (steps) is expected to occur when surface diffusion of adsorbed species is significantly lower (higher) compared to the deposition flux and is observed at higher (lower) fluxes and lower (higher) substrate temperatures. Here, we report an unconventional growth mode of inorganic monolayers on metallic substrates.

Using in situ ultra-high vacuum scanning tunneling microscopy (UHV STM), we investigated the chemical vapor deposition (CVD) kinetics of hexagonal boron nitride (hBN) monolayers on Pd(111). In each experiment, STM images are acquired while exposing Pd(111) to borazine (10^{-7} – 10^{-6} Torr) at temperatures 573 K and 673 K and for times up to 2500 s. The STM images reveal the nucleation and growth of two-dimensional islands on the Pd surfaces. From the images, we measure the areal coverage, island sizes, and island density as a function of time, temperature, and borazine flux. We find that the rates of areal coverage and island density increase ten-fold with increasing borazine pressure from 10^{-7} to 10^{-6} Torr at 573 K and three-fold with increasing temperature from 573 K to 673 K and borazine

pressure of 10^{-7} Torr. Our STM images reveal an unusual nucleation and growth mode: at lower deposition flux and higher temperature, islands form on terraces; increasing the flux and/or lowering the temperature result in preferential nucleation and growth at the step edges. Interestingly, the step-edge growth of borazine islands is observed on *both* up and down steps. We attribute this phenomenon to the structure and the highly anisotropic bonding of borazine on Pd(111). Our results provide new insights into the growth dynamics of two-dimensional layered materials.

3:20pm **SS+EM+PS+TF-ThA4 Redox-Active Ligands for Single-Site Metal-Organic Complexes on Surfaces as Heterogeneous Catalysts**, ***Tobias Morris,*** Indiana University*; D.L. Wisman,* Indiana University, NAVSEA Crane*; I.J. Huerfano, N.A. Maciullis, K.G. Caulton, S.L. Tait,* Indiana University

The utilization of single-site transition metal centers at surfaces is of growing interest in the heterogenous catalysis community. One advantage of single-site metal centers is the high dispersion so that a much higher fraction of atoms contribute to chemical activity compared to nanoparticle catalysts. Our approach to forming single-site metal centers is on-surface complexation with a redox-active ligand, which allows a high degree of ordering on the surface as well as intimate chemical contact of the metal center with the support surface. The ligand design enables us to tailor the coordination geometry and oxidation state of the metal and thus affect the cooperation between metal and ligand and the chemical reactivity. Several ligands, differing in backbone, binding pocket, design, and peripheral units were examined in this study. Tetrazine-based ligands are known for their redox activity. The on-surface two-electron redox process utilizes vapor deposition of 3,6-di-2-pyridyl-1,2,4,5-tetrazine (DPTZ) with vanadium cations onto an Au(100) surface. The metal-organic complexation leads to the growth of 1D chains consistent of one metal per ligand due to the divergent binding pockets created by the tetrazine core and pyridine rings. Exposing the V-DPTZ chains to oxygen results in a dissociative reaction of molecular oxygen to form a terminal oxo species on the vanadium, while allowing the metal-organic complex to remain intact. Interestingly, the dioxygen activation contributes adsorbed oxygen to the support surface by a spillover mechanism. The stable V-oxo species is the only oxidation product, unlike the unselective oxidation of V nanoparticles. A newly synthesized ligand, tetraethyltetra-aza-anthraquinone (EtTAAQ), utilizes a quinone backbone with adjacent pyrazine rings to generate four symmetric binding pockets. Quinones are one of the oldest studied redox-active ligands. EtTAAQ has the capacity for up to a four-electron reduction, enabling the possibility for multiple metal sites per ligand. Continued work on redesigning ligands is showing promise in increasing the cooperativity of the ligand and the metal which could lead to heightened reactivity.

4:00pm **SS+EM+PS+TF-ThA6 Oxidation and Ablation of HOPG Using Supersonic Beams of Molecular Oxygen Combined with STM Visualization**, ***Ross Edel,*** *T. Grabnic, B. Wiggins, S.J. Sibener,* University of Chicago

Graphite is widely studied due to its importance in high-performance materials applications such as high velocity flight systems as well as its key role as a model system for other carbonic materials such as graphene and carbon nanotubes. Our research focuses on the reaction of highly oriented pyrolytic graphite (HOPG) with molecular oxygen, the mechanism of which is not yet fully understood. Utilizing a one-of-a-kind instrument that combines a supersonic molecular beam and scanning tunneling microscope (STM) in ultra-high vacuum, we are able to tightly control the energy and angle of impinging oxygen and examine the nanoscopic and mesoscopic evolution of the surface. We have found that different oxygen energies, incident angles, and surface temperatures produce morphologically distinct etching features: Anisotropic channels, circular pits, and hexagonal pits faceted along crystallographic directions. The faceted and circular etch pits were formed at low O_2 energy, with faceting only apparent below a critical surface temperature, while anisotropic etching was observed with exposure to higher energy oxygen. Comparison of low- and high-grade reacted samples show that anisotropic channels likely result from the presence of grain boundaries. Reaction probability increased with beam energy and demonstrated non-Arrhenius behavior with respect to surface temperature, peaking at around 1375 K. Beam impingement angle had only minor effects on the reaction probability and etch pit morphology. Reactivity was enhanced by natural grain boundaries and artificially created point defects, showing the critical influence of small structural imperfections. Our combination of STM imaging with well-defined and controlled oxidation conditions connects interfacial reaction kinetics with time-evolving nanoscopic surface morphology, providing new insight into the oxidation of graphitic materials under high-temperature conditions. Spatio-temporal correlations obtained in this manner shed new light on interfacial erosion mechanisms, and provide an incisive complement to the information obtained using spatially-averaged gas-surface reactive scattering measurements.

5:00pm **SS+EM+PS+TF-ThA9 DLC Films by Modified HiPIMS with Effect from Pulse Parameters on Plasma Parameters and Film Quality**, ***David Ruzic,*** *I. Haehnlein,* University of Illinois at Urbana-Champaign*; B. Wu,* Southwest Jiaotong University*; D. Barlaz,* University of Illinois at Urbana-Champaign*; B.E. Jurczyk,* Starfire Industries

Diamond like carbon (DLC) films have made waves as of late in many industries. DLC provides a high strength low friction surface with the potential for high chemical resistivity. High Power Impulse Magnetron Sputtering (HiPIMS) is a promising physical vapor deposition (PVD) that creates high ionization fractions at the substrate using high power pulses over low duty factors. The resulting high plasma densities (as high as 10^{19} m^{-3}) creates ionization fractions of sputtered material at the target surface. The increase in energy of atoms due to high ionization rates at the substrate yields higher density and smoother films. In combination with a positive polarity pulse to drive ions to the substrate surface, the DLC film hardness can be increased while producing a smoother film surface.

By introducing a larger ion flux, determined through a gridded energy analyzer, the ratio of sp^3 bonded carbon to sp^2 is presented for a multitude of parameters. This work explores not only the use of positive polarity pulses, but the effect of pulse parameters, has on film hardness and morphology. By controlling the deposition rate through pulse width and repetition rate while controlling deposition energy increases by approximately 5% in sp^3 fraction were observed while surface roughness decreased by a factor of 4 for a non-hydrogenated amorphous carbon film by just the introduction of a positive polarity pulse. Further increases are reported through fine tuning the discharge parameters while looking at plasma densities, ion fraction, surface roughness, sp^3 fraction, and hardness for DLC on silicon substrates.

5:20pm **SS+EM+PS+TF-ThA10 Adsorption and Reactions on Topological Insulators Surfaces Probed by Low Energy Ion Scattering**, ***Haoshan Zhu***[1]*, W. Zhou, J.A. Yarmoff,* University of California - Riverside

Bi_2Se_3 and Bi_2Te_3 are two-dimensional topological insulators (TIs) that have attracted intense interest in recent years. TIs are promising candidates for superconductor, spintronics and quantum computing applications due to topological surface states (TSS) that connect the conduction and valence bands. The clean $Bi_2(Se,Te)_3$ surfaces prepared under ultra-high vacuum (UHV) are terminated with Se or Te, but the termination can change if exposed to air or prepared under non-ideal conditions. The adsorption and reactions of various atoms and molecules with $Bi_2(Se,Te)_3$ have thus been studied extensively, as they can result in changes to the TSS, doping and surface reconstruction. Here, TI surfaces are exposed to Cs, Bi, and halogens (Cl_2 and Br_2) in UHV and investigated by low energy electron diffraction (LEED), work function measurements and low energy ion scattering (LEIS). It is found that Cs lowers the work function and remains stable at small coverages but becomes mobile at larger coverages. Bi grows in a quasi bilayer-by-bilayer mode with the first Bi bilayer being strongly bonded to the TI surface. Both clean TI surfaces and Bi-covered surfaces are exposed to halogens. The clean surfaces are relatively inert to halogens, but they readily adsorb onto Bi films . The Bi is etched away when the samples are lightly annealed, restoring the clean Se- or Te-terminated surfaces.

5:40pm **SS+EM+PS+TF-ThA11 Atomically Controlled Metallation of Porphyrinoid Species with Lanthanides on Surfaces**, ***Borja Cirera,*** IMDEA Nanoscience, Spain*; J. Björk,* Linköping University, Sweden*; G. Bottari, T. Torres,* Universidad Autonoma Madrid, Spain*; R. Miranda, D. Ecija,* IMDEA Nanoscience, Spain

Metallation of surface confined porphyrinoid architectures have emerged as an important research topic due to its importance for biological phenomena and potential applications including optoelectronics, nanomagnetism, sensing and catalysis.

Hereby, the in-situ design of mutant porphyrinoids, either by selection of unconventional metal centers like lanthanides or by choosing different backbones, is attracting great attention. In this talk we report our latest research regarding the metallation by dysprosium, an archetype lanthanide metal for magnetic applications, of porphyrinoid species of distinct cavity size.

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

On one hand, the deposition of Dy on top a submonolayer of fluorinated tetraphenyl porphyrin species on Au(111) affords the expression of three different Dy-derived compounds, which are identified as the: initial, intermediate and final metallated states. Importantly, the initial metallated complexes exhibit a narrow zero bias resonance at the Fermi level that is assigned to a molecular Kondo resonance with $T_k \approx 120$ K, which can be switched off by means of vertical manipulation.

On the other hand, the adsorption on Au(111) of an expanded hemiporphyrazine with 27 atoms in its internal cavity is investigated, showing a long-range orientational self-assembly. Furthermore, a spatially controlled "writing" protocol on such self-assembled architecture is presented, based on the STM tip-induced deprotonation with molecular precision of the inner protons. Finally, the capability of these surface-confined macrocycles to host lanthanide elements is assessed, introducing a novel off-centered coordination motif.

The presented findings represent a milestone in the fields of porphyrinoid chemistry and surface science, revealing a great potential for novel surface patterning, opening new avenues for molecular level information storage, and boosting the emerging field of surface-confined coordination chemistry involving f-block elements.

Thin Films Division
Room 104B - Session TF+AS+EL+EM+NS+PS+SS-ThA
IoT Session: Thin Films for Flexible Electronics and IoT

Moderators: Jesse Jur, North Carolina State University, Siamak Nejati, University of Nebraska-Lincoln

2:20pm **TF+AS+EL+EM+NS+PS+SS-ThA1 Ultraflexible Organic Electronics for Bio-medical Applications**, ***Tomoyuki Yokota***, *T. Someya,* The University of Tokyo, Japan **INVITED**

Recently, flexible electronics has much attracted to realize bio medical application for their flexibility and conformability [1-3]. To improve these characteristics, reducing the thickness of the device is very effective [4]. We have developed ultra-flexible and lightweight organic electronics and photonics devices with few micron substrates. We fabricated the 2-V operational organic transistor and circuits which has very thin gate dielectric layers. The gate dielectrics were composed of thin aluminium oxide layer and self-assembled monolayers (SAMs). Due to the very thin substrate and neutral position, our device shows the highly flexibility and conformability. The device doesn't be broken after crumpling.

And also we fabricated highly efficient, ultra-flexible, air-stable, three-color, polymer light-emitting diodes (PLEDs) have been manufactured on one-micrometer-thick parylene substrates. The total thickness of the devices, including the substrate and encapsulation layer, is only three micrometers, which is one order of magnitude thinner than the epidermal layer of the human skin. The PLEDs are directly laminated on the surface of skin and are used as indicators/displays owing to their amazing conformability as their superthin characteristics. Three-color PLEDs exhibit a high external quantum efficiency (EQE) (12, 14, and 6% for red, green and blue, respectively) and large luminescence (over 10,000 candelas per square meter at 10 V). The PLEDs are integrated with organic photodetectors and are used as pulse oximeter.

References

[1] D. Khodagholy et al., Nature Commun. **4** 1575 (2013).

[2] G. Schwartz et al., Nature Commun. **4**, 1859 (2013).

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[4] D. H. Kim et al., Nat. Mater., **9**, 511 (2011).

3:00pm **TF+AS+EL+EM+NS+PS+SS-ThA3 Molecular Surface Chemistry for Improved Interfaces in Organic Electronics**, ***Jacob W. Ciszek***, Loyola University Chicago

Organic optoelectronic devices (OLED, OFETs, etc.) contain at least one, if not multiple instances of overlayers deposited onto organic semiconductors. The generated interface is inherently flawed with issues such as non-ohmic contact, overlayer delamination, or deposition induced damage arising. Traditionally, this is addressed by physical vapor deposition of yet another layer or by reengineering the materials in the device stack. In contrast, a reaction based approach allows for a wider range of function to be installed via molecular components in an organized and oriented manner, all while take advantage the inherent reactivity of the organic molecules which comprise the semiconducting layer. We have developed this approach via a "click-like" Diels-Alder chemistry whereby prototypical acene films (tetracene or pentacene) can be appended with a variety of small molecules to form an interfacial layer only ~5 Å thick. This chemistry is then applied towards improving the metal on semiconductor contact. As a demonstration of principle, Diels-Alder chemistry is utilized to form covalent bonds linking the organic semiconductor with a deposited metal contact thereby eliminating the poor adhesion present in this system. Application of the chemistry towards contact potential shifts is presented, while work towards sensing applications concludes the talk.

3:20pm **TF+AS+EL+EM+NS+PS+SS-ThA4 Investigation of Low Temperature ALD-deposited SnO_2 Films Stability in a Microfabrication Environment**, ***Tony Maindron***, *S.M. Sandrez, N.V. Vaxelaire,* CEA/LETI-University Grenoble Alpes, France

For applications such as displays (LCD, OLED) or solar cells, it is mandatory to use Transparent Conductive Oxides (TCOs) so as to allow light to extract out of the circuit or for light harvesting, respectively. In display technology, TCOs are also studied so as to replace the silicon technology developed to make the semiconducting channel in thin-film transistors. The mainstream TCO today is indium tin oxide (ITO), (90% indium oxide and 10% tin oxide). It has the advantage of having a high conductivity and a low surface resistivity, of the order of 10 ohm/square, while having a transmittance greater than 85% over the entire visible spectrum. However, it has several drawbacks, including the scarcity of indium and the high cost associated to its extraction process, which has prompted the scientific community to look for alternative TCOs. Among all TCOs, ZnO has been widely studied as a low cost single-metal oxide alternative material to ITO, as well as its multi-metal oxide derivatives using a dedicated metal dopant to control its electrical conductivity, as for instance with Al (ZnO:Al or AZO). One issue however with ZnO films lays in their relative chemical stability to water. It has been shown that films of ZnO or AZO change their physical properties when exposed to moisture: electrical conductivity decreases, roughness can increase, and optical characteristics are modified. By extension, when ZnO-based TCOs have to be finely patterned by photolithography, their high sensitivity to water-based solutions can be a severe issue. In our laboratory, we have noticed that ZnO and AZO films made by ALD at 150 °C typically are not stable in a microfabrication process: a large decrease (~ 20 %) of AZO thickness after the development step of photoresists used to pattern the TCO film has been noticed. One way to stabilize ZnO-based compounds is to anneal the films at high temperatures. However for some dedicated applications that use fragile substrates (plastic films for flexible organic electronics for instance), such post annealing processes at high temperature (typ. > 150 °C) cannot be applied. An alternative is to explore alternative materials to AZO: we found out that SnO_2 ALD (150 °C) shows very promising features regarding the stability under a microfabrication environment, while having good electrical and optical characteristics.

4:00pm **TF+AS+EL+EM+NS+PS+SS-ThA6 Dopant Distribution in Atomic Layer Deposited ZnO:Al and In_2O_3:H Films Studied by Atom Probe Tomography and Transmission Electron Microscopy**, *Y. Wu, B. Macco,* Eindhoven University of Technology, The Netherlands; *A.D. Giddings, T.J. Prosa, D.J. Larson,* CAMECA Instruments Inc.; *S. Kölling, P.M. Koenraad, F. Roozeboom,* ***Erwin Kessels***, *M.A. Verheijen,* Eindhoven University of Technology, The Netherlands

Transparent conductive oxides (TCOs) are ubiquitous in many of today's electronic devices, including solar cells. Atomic layer deposition (ALD) is a promising method to prepare high quality TCO films due to its well-known virtues – i.e., precise growth control, excellent conformality and uniformity – combined with its damage-free character. Here we report on two types of TCO films that we have studied by a combination of atom probe tomography (APT) and high-resolution transmission electron microscopy (TEM). The aim was to get more insight into how the dopants are distributed in the films.

The first study was carried out on ZnO:Al prepared by alternating cycles of $Zn(C_2H_5)_2$ and H_2O with cycles of $Al(CH_3)_3$ and H_2O in a supercycle fashion at 250 ^oC. For this material it is known that the maximum conductivity achievable is limited by the low doping efficiency of Al. To better understand the limiting factors for the doping efficiency, the 3-dimensional distribution of Al atoms in the ZnO host material matrix has been examined at the atomic scale by the aforementioned techniques [1]. Although the Al distribution in ZnO films prepared by so-called "ALD supercycles" is often presented as atomically flat δ-doped layers, in reality a broadening of the Al-dopant layers was observed with a full-width-half-maximum of ~2 nm. In addition, an enrichment of the Al at grain boundaries was seen.

The second study involved In_2O_3:H prepared by InCp and a mixture of O_2 and H_2O at 100 ºC. This material provides a record optoelectronic quality after post-deposition crystallization of the films at 200 ºC. Since both the H dopant incorporation and the film microstructure play a key role in determining the optoelectronic properties, both the crystal growth and the incorporation of H during this ALD process were studied [2]. TEM studies show that an amorphous-to-crystalline phase transition o ccurs in the low temperature regime (100-150 °C), which is accompanied by a strong decrease in carrier density and an increase in carrier mobility. Isotope studies using APT on films grown with D_2O show that the incorporated hydrogen mainly originates from the co-reactant and not from the InCp precursor. In addition, it was established that the incorporation of hydrogen decreased from ~4 at. % for amorphous films to ~2 at. % after the transition to crystalline films.

[1] Y. Wu, A. Giddings, M.A. Verheijen, B. Macco, T.J. Prosa, D.J. Larson, F. Roozeboom, and W.M.M. Kessels, Chem. Mater. 30, 1209 (2018).

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4:20pm **TF+AS+EL+EM+NS+PS+SS-ThA7 Roll-to-Roll Processable OTFT Sensors and Amplifier***, **Kai Zhang**,* University of Oxford, Department of Materials, UK*; C.-M. Chen, B. Choubey, H.E. Assender,* University of Oxford, UK

The high flexibility and relatively low cost of organic electronics are gradually providing more possibility for their application. Compared with conventional silicon based electronics, organic electronics have relatively short lifecycles and processor speed, but they are more promising in the market of wearable and flexible devices, for example, wearable health care devices, simple memory devices and flexible displays. In recent years, some flexible and wearable sensors have been developed, e.g. skin-touching sensors embedded in a sports suit can detect the change of heart rate, blood pressure, ion concentration of perspiration, or infrared radiation from the human body.

In most sensors based on organic thin film transistors (OTFT) made to date, the semiconductors are employed directly to detect analytes. However, (1) the lifecycles of this design is short due to the low stability of organic semiconductors; and (2) any modification for selectivity needs to be compatible with the semiconductor.

In this paper, we present sensors based upon an extended floating gate in order to separate the sensory area from the semiconductor. Transistors are manufactured, using our roll-to-roll vacuum webcoating facility, using a high-throughput all evaporation process (Ding et al., 2016, Taylor et al., 2015). We have demonstrated the principle of operation of a floating gate sensor integrated with the vacuum-deposited OTFT, by means of a simple strain sensor, using ferroelectric PVDF on the extended floating gate to directly act as a sensory material. To amplify the sensor signal further, a series of current mirrors and differential amplifiers have been designed based on the properties of single OTFTs. The combination of organic amplifier and OTFT sensor will be helpful to transduce sensing signal to a suitable level for wireless signal reading from flexible devices.

Reference:

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TAYLOR, D. M., PATCHETT, E. R., WILLIAMS, A., DING, Z., ASSENDER, H. E., MORRISON, J. J. & YEATES, S. G. 2015. Fabrication and simulation of organic transistors and functional circuits. *Chemical Physics,* 456**,** 85-92.

4:40pm **TF+AS+EL+EM+NS+PS+SS-ThA8 Functionalization of Indium Gallium Zinc Oxide Surfaces for Transparent Biosensors***, X. Du, S. John, J. Bergevin, **Gregory Herman**,* Oregon State University

Amorphous indium gallium zinc oxide (IGZO) field effect transistors (FETs) are a promising technology for a wide range of electronic applications including implantable and wearable biosensors. We have recently evaluated the functionalization of IGZO back channel surfaces with a range of self-assembled monolayers (SAM) to precisely control surface chemistry and improve stability of the IGZO-FETs. The SAMs evaluated include, n-hexylphosphonic acid (n-HPA), (3,3,4,4,5,5,6,6,6-nonafluorohexyl) phosphonic acid (FPA), and (3-aminopropyl) trimethoxysilane (APTMS). A comparison of the surface chemistry is made for bare and SAM functionalized IGZO back channel surfaces using X-ray photoelectron spectroscopy and electronic device measurements in air and phosphate buffer solution (PBS). We find significantly improved device stability with the SAMs attached to the IGZO back channel surface, both in air and PBS. We related this to the reduction of traps at the back channel surface due to SAM passivation. To further evaluate the IGZO-FETs as biosensors we have immobilized glucose oxidase (GOx) to the APTMS functionalized IGZO back channel surface using glutaraldehyde. We find that both the FPA functionalized and the GOx immobilized surfaces are effective for the detection of glucose in PBS. Furthermore, the GOx immobilized IGZO-FET based glucose sensors have excellent selectivity to glucose, and can effectively minimize interference from acetaminophen/ascorbic acid. Finally, we will discuss fully transparent IGZO-FET based glucose sensors that have been fabricated directly on transparent catheters.These results suggest that IGZO-FETs may provide a means to integrate fully transparent, highly-sensitive sensors into contact lenses.

5:00pm **TF+AS+EL+EM+NS+PS+SS-ThA9 Large Area Atmospheric Pressure Spatial ALD of IZO and IGZO Thin-film Transistors***, C. Frijters, I. Katsouras, A. Illiberi, G. Gelinck,* Holst Centre / TNO, Netherlands*; **Paul Poodt**,* Holst Centre / TNO and SALDtech B.V., Netherlands

Atmospheric pressure Spatial ALD is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. An emerging application for Spatial ALD is flat panel (OLED) display manufacturing. Examples include oxide semiconductors and dielectric layers for use in thin-film transistors (TFT’s), and thin-film encapsulation for flexible OLED displays. As today’s displays are fabricated on glass plate sizes in the order of several square meters, a remaining challenge is the development of large-area Spatial ALD deposition technology that is able to combine high throughput with uniform performance across very large areas.

We are developing large area Spatial ALD technology, and as a first step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm^2 sized substrates. With this tool we are able to deposit uniform films across a deposition width of 400 mm and thickness non-uniformities of ~ 1%. The whole tool is operated under an atmospheric pressure but inert N_2 environment. The tool can be used to deposit a variety of materials using both thermal and plasma-enhanced Spatial ALD.

We will present about the fabrication and performance of 30 cm x 30 cm TFT backplanes with $InZnO_x$ (IZO) and $InGaZnO_x$ (IGZO) oxide semiconductors deposited by spatial ALD. The IZO and IGZO films were deposited by plasma enhanced Spatial ALD using co-injected In-, Ga- and Zn-precursors and an atmospheric pressure N_2/O_2 plasma. The deposition process has been optimized in terms of film composition and electrical properties on a lab-scale reactor before being translated to the large area spatial ALD rector. We will report on the yield and performance of the 30 cm x 30 cm TFT backplanes, including electrical properties such as the field effect mobility, V_{on} and bias stress stability and compare it with state-of-the-art sputtered IGZO TFT’s. Finally, the challenges in up-scaling Spatial ALD to plate sizes of 1.5 m and beyond will be discussed.

5:20pm **TF+AS+EL+EM+NS+PS+SS-ThA10 Thin Film Ink-Jet Printing on Textiles for Flexible Electronics***, **Jesse Jur**, I. Kim, H. Shahariar,* North Carolina State University

Inkjet printing of thin film flexible electronics on textiles is an emerging field of research with advances in wearable technology. In this study we describe for the first-time a reliable and conformal inkjet printing process of printing particle free reactive silver ink on textile surfaces. Reactive silver ink is printed on fibers with eclectic polymers ranging from polyester and polyamide, and different structures of textiles such as knitted, woven, and nonwoven fabrics. The conductivity and the resolution of the inkjet-printed tracks are directly related to the fiber structures in the fabrics. Multiple passes of printing layers are needed to confirm the percolation of the metal network on porous, uneven surfaces. The conformity and the electrical conductivity of the inkjet-printed conductive coating on PET textiles are improved by in-situ heat curing the substrate during printing and surface modification, for example, by atmospheric oxygen plasma treatments. The in-situ heat curing potentially minimizes wicking of the ink into the textile structures. We have achieved the minimum sheet resistance of 0.2 Ohm/sq on polyester knit fabric, which is comparable to the conductive thick-paste used in the screen-printed process, as well as other traditional physical and chemical deposition processes on textile fabrics/yarns. Additionally, we have constructed textile knit structures which changes electric percolation depending on structural deformations of the knit loops, providing positive and negative gauge factors upon

stretching. The printed patterns are post-treated with diluted silicone/UV curable aliphatic water-soluble polyurethane coating to improve the durability during washing. These findings open up the possibility of integrating inkjet printing in the scalable and automated manufacturing process for textile electronic applications.

5:40pm **TF+AS+EL+EM+NS+PS+SS-ThA11 Flexography Oil Patterning for In-line Metallization of Aluminium Electrodes onto Polymer Webs: Commercial Roll to Roll Manufacturing of Flexible and Wearable Electronics***, **Bryan Stuart**, T. Cosnahan, A.A.R. Watt, H.E. Assender,* University of Oxford, Department of Materials, UK

Vacuum metallisation of aluminium through shadow masks has been commercially used for decades for depositing electrodes on rigid semiconductor devices, however recent developments have enabled large area, continuous deposition of patterned metallization in the aesthetic printing industry and has the potential for electrode interconnects for devices on flexible substrates such as Polyethylene Terephthalate (PET) and Polyethylene Naphthalene (PEN). Flexible polymer webs of PET were coated (*SeeSupplementary Figure*) with 50 nm thick, 165 um wide aluminium electrodes by commercially compatible manufacturing at roll-to-roll web speed of 2.4 m min^{-1} showing tremendous potential for large scale manufacturing of wearable electronic devices in transistors, low level energy generation (Thermoelectric generators), energy storage (thin film batteries) or display technologies (LED displays) [1].

The in-line patterning process relies on adaptation of flexography ink printing which typically transfers ink to a rubber patterned plate for printing images onto polymer webs. The flexibility of the printing plate accommodates for irregularities in the surface of the substrate making this process desirable for large area manufacturing. Metallization has been used to deposit aluminium onto a flexography applied pattern by replacing ink with a low vapor pressure oil (e.g. Perfluropolyether, Krytox®). The radiative heating of aluminium metallization causes simultaneous evaporation of the oil pattern, thereby rapidly forming the desired metal pattern onto the un-patterned regions. Currently we are scaling-up the oil flexography/metallization process into an industrial-scale roll-to-roll coater with potential web widths of 350 mm and roll speeds of 100 m min^{-1}, in order to increase web speeds, and to expand the range of materials deposited and the functional devices to which they are applied.

This paper reports on in-line pattern deposition of aluminium and other materials as applied to functional devices, for example organic thin film transistors and thermoelectric devices. In particular we are able to demonstrate how the process can be compatible with other functional layers. We will report our studies of electrode precision (shapes/sizes) by patterned metallization and our first studies of sputtering with flexography patterning. The long term view is integration of this technology along the R2R production path for single pass/high speed production of low cost and flexible integrated circuits.

References

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Thin Films Division
Room Hall B - Session TF-ThP
Thin Film Poster Session

TF-ThP2 Investigation of Target State by Plasma Emission and Target Voltage Measurements for Reactive Sputtering of Ni oxide thin films with water vapor injection, ***Yuki Yokoiwa**, Y. Abe, M. Kawamura, K.H. Kim, T. Kiba,* Kitami Institute of Technology, Japan

Reactive sputtering is one of the most commonly used techniques for obtaining compound thin films. It is well known that target mode change is very important in reactive sputtering, because the change in the target surface state induces drastic changes in the deposition rate. In the previous study, we reported that the reactive sputtering with substrate cooling and water vapor injection was promising technique to obtain Ni oxide thin films with high-rate deposition. We speculated that the high deposition rate was realized by metallic target state. In the present study, we investigated the target state in more detail using plasma emission spectroscopy and target voltage measurements.

Ni oxide thin films were formed by a RF magnetron sputtering system. Substrate temperature was varied from room temperature (RT) to -80 °C. Ni metal target was sputtered in Ar and H_2O sputtering gas atmosphere, and the flow ratio ($H_2O/(H_2O+Ar)=RH_2O$) was varied from 0 to 100%. H_2O was injected onto the target surface. Target voltage and plasma emission spectrum were measured to investigate the target surface state during sputter deposition. Film thickness was measured using a stylus profiler. The deposition rate was calculated from the film thickness and sputtering time. The optical and electrical properties of the films were studied by UV-Vis spectroscopy and four-point prove method.

At RT, deposition rate decreased from 15-20 nm/min to 4 nm/min above RH_2O=20%. On the contrary, at -80 °C, deposition rate increased monotonously with increasing RH_2O, and a maximum deposition rate of 35 nm/min was obtained at RH_2O=50%, which was approximately 8 times larger than that at RT. Corresponding to the change of the deposition rate, target voltage decreased abruptly from 330 V to 190 V above RH_2O=20% at RT when RH_2O was increased gradually. In contrast, target voltage maintained a high value of 290-330 V at -80 °C. Plasma emission spectra indicated that emission peaks due to Ni atoms disappeared at RT above RH_2O=20%, however, the peaks were clearly observed regardless of the change of RH_2O at -80 °C. These results indicate that the Ni target changed from metallic mode to oxide mode above RH_2O=20% at RT, however, metallic target mode was maintained at -80 °C.

The optical and electrical properties of the films were studied. The films deposited at substrate temperatures of RT and -80 °C below RH_2O=10% have metallic character. And transparent and insulating Ni oxide films were obtained above RH_2O=20% at both the substrate temperatures.

In summary, reactive sputtering of Ni oxide thin films in metallic target mode was realized using substrate cooling and water vapor injection.

TF-ThP3 Rectification and Non-linearity in Ferroelectric Tunnel Junction based on $BiFeO_3$ Ultra-thin Film, ***Taekjib Choi**,* Sejong University, Republic of Korea

Intriguing polarization-mediated charge transport phenomena has driven extensive research on ferroelectric resistive memories, such as ferroelectric tunnel junction, switchable diode, and ferroelectric memristor. Recently, ferroelectric tunnel junction exhibited higher on/off ratio and lower power consumption. However, to realize high density memory devices that are compatible with cross-point stack structures, it requires high rectification and high non-linearity to prevent unwanted leakage current paths through neighboring cells (a well-known sneak path problem) in cross-point structures. In this study, we fabricated the ferroelectric tunnel junction memory device for application to highly integrated vertical memory devices. The charge conduction behavior with switching of ferroelectric polarization in $BiFeO_3$ ultra-thin films based tunnel junctions were investigated. In addition, by introducing space charge layer in ferroelectric tunnel junctions, we demonstrated enhanced rectification and non-linearity in current-voltage characteristics for Pt/$BiFeO_3$/Nb-$SrTiO_3$ tunnel junctions. It was found that on /off ratio reached to maximum 10^4. Therefore, our ferroelectric tunnel junctions showing both high resistance ratio and nonlinearity factor offers a simple and promising building block of high density non-volatile memory. This research was supported by the MOTIE (Ministry of Trade, Industry & Energy (#10080643) and KSRC (Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.

TF-ThP7 Optical and Electrochemical Properties of Rhodium Oxide Thin Films prepared by Reactive Sputtering in O_2 or H_2O Atmosphere, ***ChanYang Jeong**, Y. Abe, M. Kawamura, K.H. Kim, T. Kiba,* Kitami Institute of Technology, Japan

Platinum group metal oxides, such as iridium (Ir) oxide, ruthenium (Ru) oxide, rhodium (Rh) oxide have been studied for electrochemical applications, because of their high chemical stability and electrical conductivity. However, reports on Rh oxide thin film were very scarce compared to Ir oxide and Ru oxide thin films. In this study, we investigated density, structure and optical properties of Rh oxide thin films and their effects on electrochemical properties.

Rh oxide thin films with a thickness of 100 nm were prepared by sputtering a Rh metal target in O_2 or H_2O atmosphere on glass, Si, and ITO-coated glass substrates. The substrate temperature was varied from -20 to 130 °C using a Peltier device. The density of the films was measured by X-ray reflectivity (XRR). Crystal structure and chemical bonding state of the films were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR), respectively. Optical properties were measured by UV-Vis spectroscopy. Electrochemical properties of the Rh oxide thin films were measured in 1M KOH aqueous electrolyte.

From the XRR measurements, the density of the films deposited in H_2O atmosphere was found to be lower than that deposited in O_2. The density of the films decreased with decreasing substrate temperature and the lowest density of 4.2 g/cm^3 was observed for the film deposited at -20 °C in H_2O atmosphere. XRD pattern showed that all the films except for the film deposited at 130 °C in O_2 atmosphere were amorphous. From the FT-IR spectra, absorption peaks of Rh-O and O-H bonds were observed on all the films. Higher transmittance was obtained for the films deposited in H_2O atmosphere compared to that the of films deposited in O_2. It was also found that the transmittance of the films increased with decreasing the substrate temperature, which suggests that the films were partially hydrated. As a result of the cyclic voltammetry measurements, the larger transferred charge density (ΔQ) was obtained for the films deposited in the H_2O atmosphere compared to that of the films deposited in O_2. And the largest ΔQ of 13 mC/cm^2 was obtained for the film deposited at -20 °C in H_2O atmosphere.

In summary, it was found that the Rh oxide thin film deposited at -20 °C in H_2O atmosphere had the lowest density and showed the highest electrochemical activity.

TF-ThP8 Interfacial Self-assembled Monolayers as Copper Diffusion Barrier for IGZO Semiconductor Thin Film Transistor, ***Sung-Eun Lee**, K.-H. Lim, J. Park, J.-E. Huh, J. Lee, E.G. Lee, C.I. Im, Y.S. Kim,* Seoul National University, Republic of Korea

Copper (Cu) is used in many electrode industrials because of its relatively low resistance and cost competitiveness compared to other metals. Particularly, since semiconductor and display devices require low-resistance electrodes with a high integration, interest in Cu has been more increasing. On the other hand, due to the inherent diffusion tendency, it is known that the Cu ion can easily migrate into Si or oxide based semiconductor and generate reactant with a high resistance at the interface. Thus, deterioration such as hump or abnormal current phenomenon may be occurred. To alleviate the disadvantages, diffusion barriers such as Mo, Ti and various metal alloys with hundreds of nanometer-thick or more have been used so far with micrometer size Cu electrode. However, because of the high integration of devices, the Cu electrode might soon be less than a few hundred nanometers, similar to the physical dimension of metal barrier mentioned above. Ultimately, it would be urgent to develop down sized diffusion barriers of less than ten nanometers in order to take advantage of Cu properly.

Self-assembled monolayer (SAM) is a thin film with a few nanometers to control surface of the material. Recently, many researchers study on SAM as a barrier to prevent migration of Cu ions and electrons onto dielectrics such as SiO_2. In this study, several functional groups of CH_3, SH, CF_3, and NH_2 SAM diffusion barriers located between IGZO and Cu were investigated in order to not only prevent migration of Cu ions, but also transfer electrons. As a result, there was no hump or abnormal current phenomenon occurring, therefore it was confirmed that the SAMs can prevent Cu ions migration and transfer electrons. The results of the TFT characteristic were measured similarly at whole functional groups, but the SAMs containing carbon in the functional groups such as CH_3 and CF_3 showed definitely superior performance in the hysteresis measurement.

We also confirmed that a few properties can be controlled by the body group chain length of the SAM verified by the hysteresis, transmission line method (TLM) and SIMS analysis. In other words, the TFT characteristics can be improved or deteriorated with body group chain length of SAM, and we found that it is very important to determine the proper length. This result is expected to have an important impact on the application of Cu electrode in semiconductor devices in the future.

TF-ThP9 Atmospheric-pressure Plasma Treatment Effect of Solution-processed Aluminum Oxide Gate Insulator for Oxide Semiconductor Thin-film Transistors*, Jintaek Park, K.-H. Lim, S.-E. Lee, J.-E. Huh, J. Lee, E.G. Lee, C.I. Im, Y.S. Kim,* Seoul National University, Republic of Korea

Solution-processed thin-film transistors (TFTs) have received great attention as a next generation display manufacturing method, because they do not require cumbersome equipment compared to the vacuum process and can be applied to the roll-to-roll process. Therefore, oxide semiconductors such as InO_x using aqueous route method have been studied in a simple and inexpensive process. However, most of the research is confined to the semiconductor thin film, and the research on the gate insulating film which is indispensable for the constitution of the TFT device is insufficient.

In general, high-k materials such as AlO_x, HfO_x, and TaO_x have been used as dielectric layers because they can provide large gate capacitance without significantly increasing gate leakage current. Among all high-k dielectric materials, AlO_x is widely used because of its low deposition temperature, low cost, and good compatibility with oxide semiconductors.

In this study, AlO_x using aqueous route method was deposited by a solution process and its characteristics were evaluated. Characteristic changes through atmospheric-pressure plasma treatment were observed by measurement of capacitance-frequency and breakdown voltage. It was observed that the frequency dependence of AlO_x capacitance was reduced by atmospheric-pressure plasma treatment. In general, the frequency dependence of the AlO_x capacitance is because of the ions in the layer limit the polarization response time. Thus, the changes of binding relationship according to plasma treatment time were analyzed by X-ray photoelectron spectroscopy (XPS). In addition, TFTs were fabricated by depositing a solution-processed InO_x with a semiconductor film, and the characteristics were evaluated. It was observed that field-effect mobility increased from 6.7 to 15.1 compared to the untreated samples. The surface roughness of the AlO_x films was investigated by atomic force microscopy (AFM). Semiconductor and gate dielectric fabrication, and plasma processing were performed in a non-vacuum environment and the process temperature was below 250 ℃

TF-ThP10 Microstructural and Electrical Properties of Ni Stanogermanides formed on $Ge_{0.92}Sn_{0.08}$ epi-layer Grown on Si(100) Substrate*, HanSoo Jang,* Semiconductor Physics Reasearch Center(SPRC), Chonbuk National Universityh, Republic of Korea

We present a comprehensive study on the microstructural and electrical properties of Ni stanogermanides formed on $Ge_{0.92}Sn_{0.08}$ epi-layer grown on Si(100) substrate. For the formation of Ni-stanogermanides, 30 nm-thick Ni film was deposited on $Ge_{0.92}Sn_{0.08}$ film, followed by rapid thermal annealing (RTA) process at the temperatures in the range of 300 – 600 °C for 30 s under N_2 ambient. Ni-rich stanogermanide ($Ni_3(Ge_{1-x}Sn_x)$) phase with cubic structure was formed after RTA at 300 °C, above which Ni-mono stanogermanide ($Ni(Ge_{1-x}Sn_x)$) was the only phase formed as a result of solid-state reaction between Ni and $Ge_{0.92}Sn_{0.08}$. The RTA process at 400 °C led to the formation of $Ni(Ge_{1-x}Sn_x)$ film having relatively uniform surface and interface morphologies, allowing the minimum value of sheet resistance. The samples annealed above 500 °C underwent the severe structural degradation of $Ni(Ge_{1-x}Sn_x)$ without maintaining film continuity known as agglomeration, resulting in a rapid increase in the sheet resistance. Regardless of RTA temperature, secondary ion mass spectroscopy (SIMS) results combined with energy dispersive X-ray spectroscopy (EDX) line profiling showed the segregation of Sn atoms near surface and interface region, indicating that the amount of Sn atoms were out-diffused during Ni-stanogermanides process. In particular, laterally confined Se atoms which were distributed along interface between $Ni(Ge_{1-x}Sn_x)$ island and $Ge_{0.92}Sn_{0.08}$ film was observed in the sample annealed at 600 °C.

TF-ThP11 Radiation Effects on Al_2O_3 Thin Films*, H.P. Zhu, X. Chen, **Zhong-Shan Zheng**, D.L. Li, J.T. Gao, B. Li, J.J. Luo,* Institute of Microelectronics of Chinese Academy of Sciences, China

The radiation response of Al_2O_3 thin films is investigated using Co-60 gamma rays and energetic Si ions. The Al_2O_3 thin film was prepared on Si substrates with ALD processes, and Al/ Al_2O_3/ Si structures were used to observe radiation effects on the Al_2O_3 dielectric film by the capacitance–voltage (C-V) technology. The results show that there are a lot of hole traps in the ALD Al_2O_3 film, which can be mainly attributed to oxygen vacancy (V_O) defects by calculation analyses based on the first-principles, and total dose effects are also apparent for the Al_2O_3 film irradiated using energetic Si ions at higher fluence levels. In particular, the combined impact of gamma rays and energetic Si ions on the Al_2O_3 film is examined at the same time, and the results suggest that electron traps can be introduced in the Al_2O_3 film due to Si ion irradiations.

TF-ThP12 Comparative Study of Erosion on Various Polymers and Composites both Coated Using a DC Magnetron Sputtering Process and Uncoated*, S. Hill, **Dorina Mihut**, A. Afshar, K.J. Culp, Z. Grantham,* Mercer University School of Engineering

Solid particle impact erosion is a progressive loss of the materials' mass that results from repeated impact of the erodent on the material surface. Materials selection for equipment working in this type of aggressive environmental conditions is a great challenge. These materials must possess some resistance to erosion and have high strength, hardness, toughness, and good corrosion resistance. It would be advantageous to select a lightweight material with good strength and corrosion resistance; however these materials are have limited resistance to impact erosion. Some examples of these types of materials are polymers and composites. However, in some cases, it is necessary to coat the polymers with a metallic coating to enhance certain properties of the materials. This study uses an impact erosion tester to study the effect of accelerated erosion on different polymers, composites, and metallic coated polymers and composites. A two phase mixture is circulated in a custom test fixture and allowed to impact test coupons at specified angles. The study uses three sand concentrations, a fixed liquid flow rate, and a constant impact angle during testing to determine the effect of the material's properties on the amount of erosion. The metallic coatings on the samples are aluminum, copper, and titanium and were deposited using DC magnetron sputtering equipment and the structures of the coatings was characterized using X-Ray diffraction.

TF-ThP13 Plasma-enhanced Atomic Layer Deposition of Molybdenum Compounds Thin Films Using $Mo(CO)_6$ with Various Plasma Gases*, Jeong-Hun Choi, S.W. Lee, C.M. Hyun, J.-H. Ahn,* Korea Maritime and Ocean University, Republic of Korea

In recent years, transition metal oxides and dichalcogenides have received much attention due to its attractive properties for a wide range of applications. Among these materials molybdenum compounds were studied most initiatively and achieved considerable progress. Meanwhile, metallic molybdenum is also widely used as conducting materials in many electronic applications. In this study, therefore, optical, structural and electronic properties of metallic molybdenum and its compounds thin films have been investigated. Plasma-enhanced atomic layer deposition (PEALD) was employed to form the uniform Mo, MoO_3, MoS_2 thin films. Especially, When $Mo(CO)_6$ was used as the precursor, different kinds of plasma gases such as O_2, H_2, H_2S and their mixtures for reactant resulted in selective growth of Mo, MoO_3, MoS_2, respectively. Basically, the ALD characteristics with each reactant were studied. The ellipsometry, raman spectroscopy, photo luminescence, X-ray photoelectron spectroscopy, scanning electron microscopy were used to examine film characteristics according to the different precursor combinations and growth conditions. Furthermore, the potential of metallic Mo as well as Mo compounds for device component was investigated.

TF-ThP14 Development of Metal Linear Evaporator for OLED Panel Mass Production of Gen.6 half and Gen. 8 lines*, Jung Hyung Kim,* Korea Research Institute of Standards and Science (KRISS), Republic of Korea*; M.S. Kang, K.S. Shin, D.M. Lim,* Fineva Co., Republic of Korea

In the OLED processes, the metal layer such as Ag, Mg, or Al need to be deposited on the substrate for forming cathode. Usually metal layer is deposited by using a sputtering method in LCD panel processes. In the OLED processes, we cannot use sputtering method because of charge damage on the organic layer from the plasma. We can use only the evaporation method for the deposition of metal layer. A point evaporator has been used for metal layer deposition in the OLED process. In Gen. 6

half mass production line, the substrate hung from the ceiling is rotated to acquire good uniformity of the deposition film. In Gen. 8 mass production line, point evaporators are arrayed and the substrate is scanned on the ceiling. These method of rotation and arrays are difficult to get good uniformity. Since the distance between evaporator and substrate is very long about 1000 mm, metal usage is very low about 10 %. Therefore, the demands of metal linear evaporator has been very high in the field of mass production lines. We developed a metal linear evaporator for OLED panel mass production of Gen 6 half and Gen. 8 lines. The heating method is an inductive heating with a few tens kHz of frequency and the crucible of one body is graphite. The distance between the evaporator and the substrate is less than 500 mm. The direction of evaporation is bottom-up. The uniformity of Ag film deposited with the deposition rate of 5 A/s is less than 5 % in the length of 900 mm. Our technology can be extended to a vertical type or top-down evaporator.

TF-ThP16 Fabrication of Mo/B_4C Periodic Films on the High Reflective Mirror for Applications in Beyond Extreme Ultraviolet Lithography*, **Chao-Te Lee**, W.-C. Chen, H.-P. Chen, M.-K. Wang,* Instrument Technology Research Center, Taiwan, Republic of China

The extreme ultraviolet lithography (EUVL) is based on all-reflective optics operating at wavelength of 13.5 nm, was been proposed the new lithographic systems for the semiconductor industry. Beyond extreme ultraviolet lithography (BEUL), the center wavelength of 6.7 nm, is also being considered as the next generation of EUVL. In this study, the absorber layer (Mo) and space layer (B_4C) materials with various complex refractive index were been used to design the periodic films application in BEUVL at 6.7 nm wavelength by RF magnetron sputtering system. The effects of working pressure, RF power, and substrate bias on the microstructure, roughness and optical properties of films were investigated by field emission scanning electron microscopy, X-ray diffraction, atomic force microscopy, high resolution transmission electron microscope, and EUV spectrometer. The possibility of absorber layer/space layer periodic films application for BEUVL optical device with high reflectance was also investigated.

TF-ThP17 Effects of the Electric Field Application for the Photocatalytic Property of TiO_2/Ni Thin Films*, **Taishi Segawa**, I. Takano,* Kogakuin University, Japan

In recent years, titanium oxide (TiO_2) has been attracting attention by its various properties and has been studied in a wide field such as application to solar cells or medical instruments. One of the reasons why TiO_2 is the superior material as a photocatalyst is that the photo-excited state is very stable and does not cause autolysis. Therefore TiO_2 irradiated with ultraviolet rays can make the electrolysis of water stably proceed. On the other hand, the inferior point of TiO_2 is that the absorption wavelength is limited to the ultraviolet region under 380 nm. Therefore, many researchers have studied to improve the efficiency of the light reaction of TiO_2. The distinctive point of our study is the energy supply of electricity with the light irradiation. In this report, the optimum conditions of each film thickness and applied voltage were examined.

In this study, the glass substrates of 15 × 9 mm cleaned by an ultrasonic cleaner with acetone for 5 minutes were used. The TiO_2/Ni thin films were prepared by the multi-process coating apparatus with magnetron sputtering sources. The TiO_2 thin film preparation was carried out by sputtering a Ti target introducing an Ar and an O_2 gas. An Ar gas and an O_2 gas flow rate were set to 1.5 sccm and 20 sccm, respectively. The glass substrates were heated to 200 degrees by an infrared heater. The film thicknesses of TiO_2 were changed with 0 - 200 nm and Ni were changed with 25 - 100 nm to investigate the suitable condition.

The crystal structure of each thin film was analyzed by X-ray diffraction. Optical properties were measured using a UV-Visible spectrophotometer. The photocatalytic properties were measured by a methylene-blue immersion test under irradiation of the artificial sunlamp (visible light) for 2 hours. The change of the methylene-blue transmittance was measured using a UV-Visible spectrophotometer.

In this study the change of the methylene-blue transmittance was regarded as the effect of photocatalytic characteristics. The transmittance of a voltage application showed 8 times from 4 times as compared with the case of an unapplied voltage. The transmittance of a methylene-blue solution for the TiO_2/Ni (200/100) thin film showed the highest value of 48 % by a voltage application. On the other hand, the applied voltage dependence of the TiO_2/Ni (200/100) thin film showed the highest value at 2.0 V in an applied voltage. Over 2.0 V of an applied voltage, the transmittance of a methylene-blue solution gradually decreased. It was considered that the recombination of electrons and holes was delayed by applying a voltage of an appropriate value.

TF-ThP18 Crystallization Behavior and Thermal Stability of Zr-based Metallic Glasses*, J.S. Park, D.H. Song, **JinKyu Lee**,* Kongju National University, Republic of Korea

Metallic glasses have attracted significant attention over recent year because of their unique properties such as high strength, superior magnetic properties and super-plasticity. Since the metallic glasses crystallize by a nucleation and growth process, crystallization process offers a unique opportunity of study under controlled conditions of the growth of crystals. It also provides information of the relative thermal stability of metallic glasses. As well as, study on the crystallization behavior of metallic glasses will help to control and optimize the properties of metallic glasses. Recently, for practical applications, thin film metallic glass coating by sputter deposition seems to be an alternative way for the application of metallic glass.

In this study, we report the thermal stability and crystallization behavior of Zr-based metallic glasses. Zr-based metallic glasses were fabricated by melt spinning and RF magnetron sputtering, respectively. Structural characterization of metallic glasses was investigated by X-ray diffractrometry, scanning electron microscopy and transmission electron microscopy. Thermal stability was investigated by differential scanning calorimetry during the continuous heating and isothermal annealing modes in the supercooled liquid region. Mechanical properties were determined by nano-indentation experiments using the continuous stiffness measurement method.

TF-ThP19 The Investigation of the Chemical State of the PTFE Surface Treated by Ar Plasma*, **Koki Iesaka**, I. Takano,* Kogakuin University, Japan

Polytetrafluoroethylene (PTFE) has excellent characteristics such as low friction coefficient, flame retardancy, electrical insulation, chemical resistance, etc. By utilizing these characteristics, PTFE is applied in various fields such as semiconductors, chemical plants, automobiles, etc. Furthermore, improvement of water repellency or hydrophilicity for PTFE leads to development of a new material with high-performance characteristics or a wider application.

In this study, two types of PTFE were used as samples. Those were a fluororesin adhesive tape (NITTO) referred as T-PTFE in this paper and a NAFLON sheet (NICHIAS) referred as N-PTFE. The experimental conditions were 120 - 1200 s in an irradiation time and 50 - 200 W in an RF input power of Ar plasma under an ultimate pressure of < $6.0x10^{-6}$ Pa. The observation of the surface morphology was carried out by a laser microscope (OLS 4500; OLYMPUS Co. Ltd.) and a field emission Auger micro probe (JAMP-9500F; JEOL Ltd.). The determination of the surface characteristics was carried out using a contact angle meter (DM-300; Kyowa Kaimen Kagaku Co. Ltd.) about a contact angle of water and X-ray photoelectron spectroscopy (ESCA-K1S; SHIMADZU Co. Ltd.) about a surface chemical state.

In the case ofN-PTFE, the surface C and O atomic concentration measured by X-ray photoelectron spectroscopy gradually increased until 120 s in an Ar plasma treatment time. Over 120 s those concentration gradually decreased and approached those of the untreated N-PTFE at 600 s. On the other hand, from the contact angle measurement of water, the surface characteristic gradually changed to hydrophilicity until 120 s as compared to the untreated N-PTFE. It was considered that the CF_2 bonds of PTFE which induced water repellency decreased by preferential sputtering of F and the free bonds of C absorbed O_2 of the air or H_2O.

The large treatment energy such as ion beams caused the formation of the needle-like morphology, while the low energy of Ar plasma changed only a chemical state regardless of a treatment time. It became clear that the treatment energy for the stable polymer like PTFE influenced the chemical state or the morphology.

TF-ThP20 The Influence of ZnO Layers for Photovoltage of Cu_2O/ZnO/TiO_2 Thin Films Prepared by Reactive Sputtering*, **Keisuke Ishizaka**,* Kogakuin University,Japan*; I. Takano,* Kogakuin University, Japan

As one of solution methods of the power shortage and global warming, a renewable energy such as solar cells is desired. In addition the high purity silicon that is the main raw material for solar cells is insufficient worldwide, and so new solar cells without silicon that are able to be replaced to silicon-

based solar cells have been required. Practical application of oxide-based thin film solar cells is expected in reduction of the energy cost or the environmental load.

Generally a typical oxide-based thin film solar cell is known as a wet dye-sensitized solar cell composed of an electrolyte, an electrode of a titanium oxide and a sensitizing dye. Recently a solid-state dye-sensitized solar cell which uses metal oxides instead of an electrolyte has been studied. In our previous study on Cu_2O/TiO_2 solid-state dye-sensitized solar cells, the main problem was Cu diffusion from a Cu_2O layer to a TiO_2 layer. Because the diffusion of Cu to a titanium oxide layer induces the collapse of p-n junction, various materials as an intermediate layer between Cu_2O and TiO_2 have been attempted.

The ZnO layer used in this study has characteristics of a transparent oxide semiconductor, a low electrical resistivity or an n-type semiconductor. Especially the ZnO layer show a lower value about an electrical resistivity than the NiO layer or the TaON layer which had been used in the previous study.

$Cu_2O/ZnO/TiO_2$ solar cells were fabricated by reactive magnetron sputtering. As substrates, the EAGLE XG glass and the ITO-film coated glass were ultrasonically cleaned by acetone. The oxide layers were deposited on those substrates by using pure metals as a sputtering target material in an oxygen gas atmosphere. The flow rate of an argon gas for sputtering was kept at 15 sccm of Cu_2O, and at 20 sccm of TiO_2 and ZnO. The flow rate of an oxygen gas for sputtering was kept at 1.5 sccm of TiO_2, and at 10 sccm of Cu_2O and ZnO A thickness of a TiO_2 and a Cu_2O layer was kept at 200 nm, while a thickness of the ZnO layer was changed from 2 nm to 50 nm. $Cu_2O/ZnO/TiO_2$ solar cells were successfully fabricated by reactive magnetron sputtering. The investigation of $Cu_2O/ZnO/TiO_2$ solar cells were carried out by an x-ray diffraction, a spectrophotometer and a field emission Auger microprobe.

TF-ThP21 The Formation of Amorphous Carbon Thin Films by Ion Beam Mixing*, Kenji Iwasaki, I. Takano,* Kogakuin University, Japan

Recently, single-layer graphene sheets, diamond films or carbon nitride films have attracted attention as high-functional materials containing carbon. Among them, Diamond-Like Carbon (DLC) is an amorphous carbon film showing superior characteristics which are close to diamond. Since those characteristics are high hardness, low friction coefficient, etc., amorphous carbon is used in a wide range of mechanical fields such as machine parts or engine parts. On the other hand, as new characteristics of amorphous carbon, the gas barrier or the biocompatibility is studied and amorphous carbon is also applied to food containers or medical instruments.

Amorphous carbon films are fabricated by various methods such as physical vapor deposition or chemical vapor deposition. Because almost amorphous carbons have the high internal stress, the adhesion between the formed carbon film and the substrate became often a important problem. In our studies, amorphous carbon films have been formed by using the ion beam irradiation in a hydrocarbon gas atmosphere to improve the adhesion between the carbon film and the substrate. Generally it is known that the mixing layer in interface of a substrate is formed by high energy ions. In the experiment of the ion beam mixing method, the multi-process coating apparatus with a mass analyzer of 45 degrees in a beam line from the Freeman type ion source was used. C_2H_2 used as an atmosphere gas has a higher deposition rate than other hydrogen gases such as ethylene (C_2H_4) or methane (CH_4).

In the experiment, an N^+ or an N_2^+ ion beam was irradiated in a C_2H_2 atmosphere to various substrates (Stainless steel, Al, Cu, Si) at conditions of 20 kV in an ion energy and of 2 - 10 mA/cm^2 in an ion current density. Obvious depth profiles of N element was obtained by a field emission Auger micro probe, while the slight deposition of amorphous carbon on the surface of each substrate was observed regardless of a value of an implanted N element.

TF-ThP22 Enhancing Ultra-violet Optical Properties of Aluminum Mirrors with a Single Step Approach to Oxide Removal and Fluorine Passivation*, David Boris,* U.S. Naval Research Laboratory*; A.C. Kozen,* ASEE Postdoctoral Fellow*; J. del Hoyo, M.A. Quijada,* NASA Goddard Space Flight Center*; S.G. Walton,* U.S. Naval Research Laboratory

Astronomical measurements in the Far Ultra-violet (FUV, 90-200nm) have typically relied on aluminum thin films due to aluminum's high reflectivity over this wavelength range. Unfortunately, the native aluminum oxide layer formed in atmosphere is strongly absorbing in this wavelength range, requiring that the aluminum films be passivated with a dielectric that inhibits oxidation. Due to the fast oxidation of aluminum, a simultaneous etch and deposition process is required to both eliminate the native aluminum oxide after growth and replace it with a different passivation coating layer. Optical measurements in the FUV range are some of the most challenging due to limited selection of low reflectivity coatings available for use on aluminum thin films. Typically magnesium fluoride (MgF_2) or lithium fluoride (LiF) coatings are used for these passivation purposes but each has its problems. MgF_2 has an absorption cutoff at 115 nm occluding a critical part of the FUV spectrum. LiF has a lower absorption cutoff at 102.5 nm, but is hygroscopic and thus susceptible to degradation in ambient conditions. A promising alternative to these coating materials is AlF_3, which theoretically can provide reflectivity greater than 50% down to 100 nm if the coating is sufficiently thin. In this work, we explore the use of electron beam generated plasmas to simultaneously etch the native oxide layer from aluminum thin films while depositing an AlF_3 capping layer to passivate the aluminum reflector. XPS measurements indicate that this approach is cable of producing very thin (<5 nm) AlF_3 films with some mild oxygen contamination. We will discuss the impact of plasma power, chemistry, and time on the composition and structure of the passivating layer and its subsequent optical properties.________________________________* This work partially supported by the Naval Research Laboratory Base Program

TF-ThP24 Using a Semitransparent Underlayer to Determine Optical Constants of a Mostly Opaque Layer by Thin Film Interference: Application to AlF_3 on Al in the Extreme Ultraviolet*, Gabriel Richardson,* *K.M. Wolfe, M.D. Barona, R.S. Turley, D.D. Allred,* Brigham Young University

The presence of interference fringes in thin-film reflectance and transmission are invaluable in obtaining thicknesses and optical constants of thin-film materials. When a material is highly absorbing, however, interference fringes may not be produced. One particularly noteworthy technique to deal with this complication in and near the visible range is to place a transparent layer beneath the semitransparent thin-film whose optical properties are to be determined. (Hilfiker, et al.) A portion of the light passing through the film, reflecting off the substrate and then, transmitting again through the film, interferes with the front-surface reflected light producing interference fringes whose position depends on the layers' thicknesses and indices, and the light's wavelength and angle of incidence. The damping of the fringes also highly constrains the optical constants of the overlayer. We have extended this approach into the extreme ultraviolet to obtain the optical constants of aluminum fluoride between 17.1 and 49.5 nm using evaporated aluminum as the "transparent" interference layer. The aluminum fluoride is evaporated within minutes after the aluminum and without breaking vacuum so as to minimize the presence of oxygen on the aluminum film. The AlF3 also acts as a barrier layer, drastically retarding the oxidation of the aluminum film after it is removed from the deposition system. Complications associated with obtaining the AlF3 EUV constants include: first, the fact that the aluminum layer is not perfectly transparent, and second that, in some cases, there is an ultrathin film of aluminum oxide on the Al which formed before the barrier is deposited or forms gradually with time afterwards. In fact, it is in probing the time evolution of such oxide layer thicknesses that the technique has the promise of becoming particularly useful for studying barrier layers for broadband Al mirrors. Hilfiker, James N.; Singh, Neha; Tiwald, Tom; et al., "Survey of methods to characterize thin absorbing films with Spectroscopic Ellipsometry," THIN SOLID FILMS, 516(22), (2008) 7979-7989.

TF-ThP25 Thermoelectric Properties of Sb_2Te_3 Thin Films*, Eshirdanya McGhee,* *B. Bohara, C. Payton, S. Gere, S. Budak,* Alabama A&M University

The efficiency of the thermoelectric materials (figure of merit, ZT) that found to be limited in bulk structures has shown an enhancement by introducing nanostructures such as nanowires, multilayers, and nanocomposites. ZT relies on the Seebeck coefficient (S), the electrical conductivity (σ) and thermal conductivity (K). Nanostructure thin films have shown enhancement in ZT then bulk thermoelectric materials. DC/RF magnetron sputtering technique was utilized to fabricate nano-scale thin films of antimony telluride (Sb_2Te_3) on SiO_2 substrates using Sb_2Te_3 target. Thermal annealing was carried out to enhance thermoelectric efficiency by forming quantum structures within the films. The Seebeck coefficient, van der Pauw four-probe resistivity, mobility, Hall coefficient, density, measurements were performed, and power factor has been found to be improved in nano-scale thin films by thermal annealing. Thermal treatment showed positive effects on the thermoelectric properties of Sb_2Te_3 thin

films on the selected temperatures. The findings will be shown during the meeting.

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TF-ThP26 Thermal Annealing Effects on the Thermoelectric Properties of CoAg Thin Films*, **Satilmis Budak**, S. Gere, E. McGhee, E. Gamble,* Alabama A&M University

Many developed countries go to the sustainable, efficient, and renewable energy sources due to the high demand in energy usage. Power generation from the thermoelectric materials is one of the promising area among the others. Efficient thermoelectric materials (TE) could convert heat into electrical energy. These materials are used as thermoelectric generators (TEG) using Seebeck effect, and thermoelectric coolers (TEC) using Peltier effect. The heat generated from TE could be used in many areas like in electrical powers, automobiles, airlines, and marine vessels. The dimensionless figure of merit, ZT, shows the efficiency of the thermoelectric materials and/or devices. ZT is calculated by multiplying the square of the Seebeck coefficient with the electrical conductivity and the temperature, then dividing it all by its thermal conductivity. DC/RF magnetron sputtering technique was used to fabricate nano-scale thin films of Cobalt-Silver (CoAg) on SiO_2 substrates using Co and Ag targets with co-deposition procedure. Thermal annealing was introduced to enhance thermoelectric efficiency by forming quantum structures within the films. The Seebeck coefficient, van der Pauw four-probe resistivity, mobility, Hall coefficient, density, measurements were performed, and power factor has been found to be improved in nano-scale thin films by thermal annealing. The findings will be shown during the meeting.

Acknowledgement

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, **NSF-**MRI-1337616, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

TF-ThP28 Interlayer Effect for Photocatalytic Properties of TiO_2/Cu_2O Thin Films Prepared by Reactive Sputtering*, **Akihiro Joichi**, I. Takano,* Kogakuin University, Japan

In recent years, various properties of TiO_2 have attracted attention and the studies have been conducted in a wide field. Particularly, in photocatalytic properties, TiO_2 have antifouling or antibacterial actions, and is applied to the outer wall of the building or the inner wall of the operating room. However, as the inferior point of TiO_2, the absorption wavelength is limited to an ultraviolet light. In the previous study, it was attempted to expand the absorption wavelength to a long wavelength by inserting a Cu_2O layer under a TiO_2 layer. On the other hand, because the photocatalytic properties of TiO_2 deteriorated by Cu diffusion from Cu_2O, a NiO layer or a TaON layer was inserted as the intermediate layer to prevent the diffusion. In this research, the effect of an inserted ZnO layer was investigated for the photocatalytic property and was compared with a NiO layer or a TaON layer.

Glass (Eagle XG) plates processed to 15 mm × 9 mm were used as substrates, and ultrasonic cleaning was performed using acetone for 5 minutes for the substrates. The multi-process coating apparatus (BC5146, ULVAC) was used to clean up the substrate by rf sputtering and to deposit the thin films of TiO_2, ZnO and Cu_2O. The deposition chamber was equipped with RF and DC sputtering cathodes. Each oxide film was formed by sputtering a Ti, a Cu or a Zn metal target in an O_2 atmosphere. The ultimate pressure of the deposition chamber was 8.0×10^{-6} Pa and deposition pressure was 0.08 Pa by introducing an Ar and an O_2 gas. Photocatalytic properties were measured by a methylene blue immersion test. In the methylene blue immersion test, a quartz cell filled by 3 ml of a methylene blue solution of 10 ppm was used and the sample immersed therein was irradiated by sterilizing light or artificial sun light for 6 hours. The chromaticity change of the methylene blue solution was measured by using a spectrophotometer at a predetermined time.

In the multi-layer thin films inserting different oxide layers, the photocatalytic measurement of the TiO_2/TaON/Cu_2O thin film showed the highest transmittance, because the optimum condition of a ZnO layer was not enough. The optimum thickness of a ZnO layer will be investigated until the conference.

TF-ThP29 The effect of Proton Radiation on ALD HfO_2 Films and HfO_2 based RRAM*, **Panpan Xue**,* University of Wisconsin-Madison*; Z. Wang,* Stanford University*; T. Chang,* University of Wisconsin-Madison*; Y. Nishi,* Stanford University*; Z. Ma, J.L. Shohet,* University of Wisconsin-Madison

The effect of proton radiation on HfO_2-based resistive-random-access-memory (RRAM) is investigated using 10 and 300-keV protons with fluences of 10^{13} and 10^{15} cm^{-2}. The I-V characteristics, set and reset voltage, forming process and HRS resistance were measured before and after irradiation. Each RRAM cell has a Pt/HfO_2/TiN metal-insulator-metal structure and a 5-nm HfO_2 deposited with ALD. All RRAM devices operated functionally after proton irradiation. However, a number (about 30%) of the 10-keV proton-exposed RRAM cells were formed and set to LRS after exposure. In addition, the HRS resistance exhibited a significant decrease after irradiation resulting from displacement damage. After a period of time at room temperature, the radiation-induced damage to the HfO_2 film recovered and the HRS resistance increased compared to the initially exposed samples. The displacement damage produces oxygen vacancies and interstitial oxygen atoms that contribute to the generation of the conductive filaments. The oxygen vacancies generated during proton irradiation at the interface can affect the forming process.

TF-ThP30 Comparison of Hafnium Oxide and Zirconium Oxide for Fabricating Electronic Devices*, **Kenneth Davis**, Z. Duncan, M. Howard, T. Wimbley, Z. Xiao,* Alabama A&M University

Thin films of hafnium dioxide (HfO_2) and zirconium oxide (ZrO_2) are used widely as the gate oxide in fabricating integrated circuits (ICs) because of their high dielectric constants. In this research, we report the growth of hafnium dioxide (HfO_2) and zirconium oxide (ZrO_2) thin film using atomic layer deposition (ALD), and the fabrication of *complementary metal-oxide semiconductor* (CMOS) integrated circuits using the HfO_2 and ZrO_2 thin films as the gate oxide. MOSFETs, CMOS inverters, and CMOS ring oscillator were fabricated, and the electrical properties of the fabricated devices were measured. The measurement results on the devices fabricated with the two films were compared, and will be reported in the Conference.

TF-ThP31 Development of the Synchrotron-based Capabilities for Direct, *In-situ* XANES/XAFS Measurements of Thermal ALD: Initial Proof-of-Concept Study Exploring ZrO_2 ALD*, **David Mandia**, B. Kucukgok, S. Letourneau, M.J. Ward, A. Yanguas-Gil, J.W. Elam,* Argonne National Laboratory

Atomic layer deposition (ALD) has become an essential tool for the design and fabrication of electronic materials key for a wide range of applications from semiconductor processing to advanced power electronics and photovoltaics. The resulting materials are characterized by thicknesses in the nm scale, they are typically amorphous and yet they exhibit unique properties that depend on growth conditions in ways that are not yet understood. As an example, ferroelectric hafnium oxide has been recently reported, achieved through the stabilization at the nanoscale of a non-centrosymmetric orthorhombic phase that is not stable at ambient pressure for bulk materials. Another example is the development of nanolaminate (NL) materials, composite thin films comprised of alternating layers of metal oxides (eg. HfO_2 and ZrO_2 in the case of ferroelectric HfO_2)that demonstrate unique optical, mechanical, and electrical properties. To this end, the stable monoclinic phase found for HfO2 has Hf-O bonds with 7-fold coordination at room temperature whereas the tetragonal phase, which is favoured for ZrO_2 at room temperature, has Zr-O bonds with an 8-fold coordination environment. The intermixing of these phases by tuning the number of ALD sub-cycles of each component – thereby changing the NL composition – can lead to non-trivial phase transformations in their local structure that deviate from their bulk composition. In this work we explore the genesis and evolution of ZrO_2 films in the first 10 ALD cycles using a custom conflat cube reactor design for *in-situ* (fluorescence mode) XANES/XAFS measurements at the Advanced Photon Source. We will present results of the direct XANES/XAFS measurement of single TDMAZr and H_2O exposures during the ZrO_2 ALD process, results of initial proof-of-principle experiments using the *in-situ* XAFS/XANESchamber and *ex-situ* XAFS/XANES results of $(HfO_2)_x(ZrO_2)_y$ NLs.

TF-ThP32 Nitridation of Transition Metal Oxide Films*, **Li Chang**, W.-L. Chen, K.A. Chiu, Y.S. Fang,* National Chiao Tung University, Hsinchu, Taiwan, Taiwan, Republic of China

Transition metal nitrides are of important industrial applications due to their good electrical conducting properties with high hardness. For

formation of the nitride films, plasma nitridation of TiO_2, HfO_2 and ZrO_2 films on Si (100) substrates has been studied with microstructural characterization of x-ray diffraction, electron microscopy,and x-ray photoelectron spectroscopy. Nitriding was performed by using microwave plasma with gas mixture of nitrogen and hydrogen. It is found that microwave plasma is efficient to transform oxide into nitride from the surfaces of the oxide films. With extended nitriding time, a nitride film can be obtained on Si. Furthermore, an epitaxial nitride film can be obtained from an oxide film which was in epitaxy with Si.

TF-ThP36 Investigation of Synthesis Yield Variation of Single-Walled Carbon Nanotubes inside Horizontal Chemical Vapor Deposition Systems*,*
G.-H. Jeong, ***Sung-Il Jo****,* Kangwon National University, Republic of Korea

Single-walled carbon nanotubes (SWNTs) have been expected to be applied to various fields such as nanoelectronic devices, transparent conducting films, energy devices and sensors due to their outstanding physical and chemical properties. A chemical vapor deposition (CVD) is the most popular method for SWNTs synthesis because of its simplicity on SWNTs synthesis process and easy control of process parameters. In general, most of the synthesis experiments have been performed in the central region of the reactor so far where temperature uniformity is guaranteed.

In this study, we report the result of detail investigation of the SWNTs synthesis yield depending on sample position in a horizontal CVD reactor. Methane and Fe thin films were used as feedstock and catalyst for SWNTs synthesis, respective ly. Ultra high resolution scanning electron microscope (UHR-SEM) was used to confirm the synthesis yield variation of SWNTs along the axial distance of the reactor. The morphology and crystallinity of the synthesized SWNTs were evaluated by atomic force microscope and Raman spectroscopy, respectively. Main result of this study shows that the highest synthesis yield of SWNTs was observed at the rear region of the reactor not the central region at all synthesis conditions. The results of this study are expected to be applicable to the synthesis of various nanomaterials using CVD process.

TF-ThP37 Optical and Mechanical Properties of Diamond-like Carbon Thin Film deposited by Filtered Cathodic Vacuum Arc Source for Durable Coating of Infrared Optics*,*
Jung-Hwan In*, M.W. Seo, H.Y. Jung, S.H. Kim, J.H. Choi,* Korea Photonics Technology Institute, Republic of Korea

Diamond-like carbon (DLC) thin film is used as a durable coating in many applications (e.g. infrared optics, mold core for glass lens, engineering ceramic, cutting tool and sliding part in the engine of vehicle). DLC thin film can be categorized according to hydrogen content and sp3 bonding content [1]. Among several kinds of DLC thin film, an a-C:H thin film containing hydrogen atoms usually has been used for IR optics [2]. In this study, it was shown that tetrahedral amorphous carbon (ta-C) thin film deposited by filtered cathodic vacuum arc (FCVA) source without hydrogen addition can be used as durable coating in far and mid-IR optics. The optical transmittance in infrared and mechanical properties by using nano-indentation were measured in various substrate bias voltage conditions. The optical transmittance and hardness decreased with the substrate bias voltage. The refractive index and extinction coefficient were estimated in 1.2 µm thick ta-C coating on a Si window. The hardness of 1.2 µm thick ta-C coating measured by using nano-indentation was about 50 GPa. In addition, the effect of CH_4 gas addition in FCVA source on optical and mechanical properties of DLC coating was investigated. It was thought that a ta-C thin film by FCVA source is appropriate as a durable coating for IR optical materials with especially high elastic modulus (e.g. silicon, germanium).

Acknowledgement

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TF-ThP38 Influence of Temperature and Plasma Gas Chemistry on Atomic Layer Epitaxial Growth of InN on GaN Assessed with *In Situ* Grazing Incidence Small-Angle X-ray Scattering*,*
Jeffrey Woodward*, S.G. Rosenberg,* American Society for Engineering Education (residing at U.S. Naval Research Laboratory)*; N. Nepal, S.D. Johnson,* U.S. Naval Research Laboratory*; C. Wagenbach,* Boston University*; A.C. Kozen,* American Society for Engineering Education (residing at U.S. Naval Research Laboratory)*; Z.R. Robinson,* The College at Brockport - SUNY*; D.R. Boris, S.G. Walton,* U.S. Naval Research Laboratory*; K.F. Ludwig,* Boston University*; C.R. Eddy, Jr.,* U. S. Naval Research Laboratory

Plasma-assisted atomic layer epitaxy (ALEp), a variant of atomic layer deposition in which relatively higher temperatures are utilized to promote surface diffusion for epitaxial growth, offers several potential advantages over conventional growth methods such as metalorganic chemical vapor deposition and molecular beam epitaxy for the epitaxy of III-N materials and device structures. These advantages include significantly lower growth temperatures and highly controlled layer thicknesses, the latter of which is the result of the sequential pairs of self-terminating and self-limiting reactions that constitute the growth process. However, ALEp is a relatively new method for III-N growth, and significant efforts will be required to better understand the nucleation and growth kinetics. To this end, grazing incidence small-angle X-ray scattering (GISAXS) has been previously utilized for the study of surface morphology during the ALEp growth of InN[1] and AlN[2] on a-plane Al_2O_3 substrates. GISAXS is a non-destructive technique that can probe electron density fluctuations on length scales ranging from approximately 1 nm to 250 nm in an integral manner[3], making it well-suited to the study of epitaxial growth. The resulting intensity distribution from a set of scattering objects is related to the form factor and structure factor, which are the Fourier transforms of functions describing the object shape and spatial arrangement, respectively.

In this work, we present data from *in situ* GISAXS studies performed at the Cornell High Energy Synchrotron Source during the ALEp growth of InN on bulk GaN substrates. Two growth parameters were investigated independently: temperature (180 °C, 250 °C, and 320 °C) and the ratio of N_2 to Ar gas flows into the plasma source (75/200, 31/244, and 15/260). The GISAXS patterns were analyzed in order to extract information about the evolving morphologies. The data indicate that InN islands nucleated with greater density at 180 °C than at 250 °C and 320 °C, and that the island density decreased as the growth progressed for all temperatures. While the initial areal densities and island diameters at 250 °C and 320 °C were approximately identical, the density and diameter of the latter exhibited more significant decrease and increase, respectively, with time, which may indicate a temperature-dependent coarsening due to island coalescence or Ostwald ripening. The gas flow ratio had minimal effect on diameter and density, but influenced the island shape.

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TF-ThP39 Water-based Superconcentrated Electrolytes as Gate Dielectric for High-performance Solution-processed Oxide Thin Film Transistors*,*
Eun Goo Lee*, K.-H. Lim, J.T. Park, S.-E. Lee, J.H. Lee, C.I. Im, Y.S. Kim,* Seoul National University, Republic of Korea

Thin film transistors(TFTs) using oxide-based semiconductors have attracted much attention because of their large field-effect mobility, low process temperature and printing process. However, most TFTs require high operation voltage due to the low capacitance of the gate dielectric, which causes a large amount of power consumption. In order to realize electronic devices with miniaturization, light-weighting and flexibility, it is necessary to study high-k dielectrics materials which enable low operation voltage. To solve this problem, several research groups are studying various materials capable of forming an electrical double layer that lowers the operating voltage by accumulating ultra-high charge carriers at the semiconductor / dielectric interface. Herein, we propose water-based superconcentrated electrolytes films as gate dielectric materials to take advantage of the low cost, safety, environmentally friendly and high dielectric constant of water. By embedding water-based electrolytes in a cross-linking polymer network by photo irradiation, we fabricated robust and flexible free-standing films that were showed high capacitance values of 6.72 ± 0.16 uF/cm^2 at 0.5 Hz. In addition, the low electrochemical stability window of conventional aqueous electrolytes has been extended from 1.2 V to 3 V, allowing stable TFT operation at ± 1 V. The device with aqueous route indium oxide semiconductor and water-based superconcentrated electrolytes film as a dielectric layer has demonstrated

an excellent electrical characteristic, including a low operating voltage (≈1 V), small subthreshold swing voltage of 110 mV/dec and the linear mobility in excess of 30.7 ± 1.6 $cm^2/V s$ at very low drain voltage (0.1 V). These findings will open the door to the use of environmentally friendly new dielectric materials for flexible and wearable devices with low-power consumption and high mobility.

TF-ThP40 Atomic Layered Deposition and Characterizations of HfO_2 for OLED Encapsulation, ***Nak-Kwan Chung***, Korea Research Institute of Standards and Science (KRISS), Republic of Korea; *S. Kim, J.Y. Yun, J.T. Kim,* Korea Research Institute of Standards and Science (KRISS)

Flexible OLED devices require encapsulation layers with low water vapor transmission rate and low temperature process. In this presentation, We report low-temperature preparation of hafnium oxides (HfO2) by atomic layer deposition (ALD). The hafnium oxide thin films were deposited from tetrakis ethylmethylamino hafnium (TEMAHf) as the Hf precursor, ozone (O3) as the reactant, and NH3 as the catalyst on 200 mm silicon wafers at substrate temperatures from 50 to 300°C. The properties of HfO2 films were investigated by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and X-ray deflection (XRD). It was found that HfO2 films grown at low temperature of 50°C using the combination of O3 and NH3 were very smooth and amorphous, and have low impurity contents.

TF-ThP41 Reaction Mechanism Study on the Atomic Layer Deposition of Titanium Oxide Film using Heteroleptic Precursors, ***Jaemin Kim***, *H.-L. Kim, J. Gu, S. Kim, H. Jung, R. Hidayat, Y. Myung, W.-J. Lee,* Sejong University, Korea

Titanium oxide has been extensively studied for various applications including the high-permittivity dielectric of DRAM capacitors, photocatalysts, and optical coatings. Atomic layer deposition (ALD) technology is replacing physical vapor deposition or chemical vapor deposition to provide excellent step coverage, accurate film thickness control, and high stoichiometry film quality. The most common titanium precursors are homoleptic precursors, such as titanium tetraisopropoxide (TTIP) and tetrakis(dimethylamino)titanium (TDMAT). In general, higher deposition temperature improves the physical and electrical characteristics of the dielectric film, such as film density, stoichiometry, and purity. However, the TTIP and TDMAT decompose at over 200°C, resulting in poor step coverage and high impurity concentration. Therefore, we need titanium precursors with excellent thermal stability together with high reactivity and sufficient volatility. It was reported that mixed alkoxide-cyclopentadienyl titanium compounds show better thermal stability than titanium alkoxides, and the thermal stability is further improved by replacing $C_5H_4(CH_3)$ (MeCp) with $C_5(CH_3)_5$ (Cp*) [1]. In the present study, we investigated the reaction mechanism of ALD of titanium oxide using heteroleptic titanium precursors with different cyclopentadienyl-type ligands. $CpTi(OMe)_3$ and $Cp^*Ti(OMe)_3$ were selected to investigate the effect of cyclopentadienyl ligand. Ozone (O_3) and water (H_2O) were compared as the oxidizing agent. Saturation dose and the ALD temperature window were determined by measuring growth rates with different precursor feeding times, oxidizing agent feeding times, and the process temperatures. The surface reaction was investigated at different temperatures by using in-situ quartz crystal microbalance, in-situ Fourier transform infrared spectroscopy, and was simulated by density functional theory calculation.

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Peng, Q.: TF+PS-ThM12, 35; TF-MoA10, **13**; TF-MoA9, 13
Pennachio, D.J.: PS+EM+TF-ThA8, 38
Perrotta, A.: PS+TF-MoM8, 3
Pesce, V.: TF+AM+EM+PS-TuM3, 14; TF+AM+EM+PS-TuM5, **14**
Petford Long, A.K.: TF+EM+MI+PS-MoA9, 11
Petit-Etienne, C.: PS+EM+TF-ThM13, 32
Phatak, C.M.: TF+EM+MI+PS-MoA9, 11
Pilz, J.: PS+TF-MoM8, **3**
Pletincx, S.: TF+SS-TuA1, **21**
Plichta, T.: TF+SS-TuA7, 22
Polat, K.G.: TF+EM+MI-WeA10, 29
Ponizovskaya Devine, E.: TF+EM+MI-WeA10, 29
Poodt, P.: TF+AS+EL+EM+NS+PS+SS-ThA9, **42**; TF2-MoM4, 8
Porter, L.M.: EM+2D+NS+PS+RM+TF-ThA4, 37
Pouladi, S.: TF-MoA4, 12
Pourtois, G.: TF+AM+EM+PS-TuM10, 15
Prokes, S.M.: TF+EM+MI-WeM6, 25
Prosa, T.J.: TF+AS+EL+EM+NS+PS+SS-ThA6, 41
Purektzy, A.: 2D+EM+MI+NS+TF-MoM5, 1
Pyeon, J.J.: TF-TuM3, 17
— Q —
Qadri, S.B.: TF-TuM4, 17
Quadrelli, E.A.: TF+AS+EL+PS-ThM10, **33**
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Rack, P.D.: TF+AS-TuM10, **16**; TF+EM+MI-WeA11, 29
Rahman, T.S.: TF+AS+EL+PS-ThM4, 33
Rai, R.H.: EM+2D+NS+PS+RM+TF-ThA3, 37
Ranjan, A.: PS+EM+TF-ThA10, 39
Rao, R.: EM+2D+NS+PS+RM+TF-ThA3, 37
Rathi, M.: TF-MoA4, 12
Rathsack, B.: PS+EM+TF-ThA10, **39**
Ravichandran, J.: TF+EM+MI-WeA8, 29
Ray, D.: TF-MoA8, 12
Reddy, P.: TF+AS+EL+PS-ThM1, 32
Redwing, J.M.: 2D+EM+MI+NS+TF-MoM1, 1; TF+AM+EM+PS-TuM6, 15
Reed, E.J.: 2D+EM+MI+NS+TF-MoM6, 2
Renaud, V.: PS+EM+TF-ThM13, **32**
Reniers, F.: PS+TF-MoM9, 3
Reuter, R.: TF+AS+EL+PS-ThM12, 33
Richardson, J.G.: TF-ThP24, **47**
Richter, C.: EM+2D+NS+PS+RM+TF-ThA4, 37
Rickard, A.: TF+AS-TuM5, 16
Riedl, H.: SE+NS+TF-MoM6, 5
Riedl, T.J.: TF-MoA1, **11**

Ritala, M.K.: TF+AS-TuM12, 16
Rivolta, N.: TF+EM+MI-WeM13, 26
Robinson, Z.R.: PS+EM+TF-ThA8, 38; TF+EM+MI-WeM6, 25; TF-ThP38, 49
Rochat, N.: PS+EM+TF-ThM13, 32
Roozeboom, F.: TF+AS+EL+EM+NS+PS+SS-ThA6, 41; TF2-MoM4, 8
Rosenberg, S.G.: PS+EM+TF-ThA8, **38**; PS+TF-MoM11, 4; TF-ThP38, 49
Roshko, A.: TF+AM+EM+PS-TuM4, 14
Rouleau, C.: 2D+EM+MI+NS+TF-MoM5, 1
Routkevitch, D.: TF+PS-ThM2, **34**
Rowley, A.H.: TF+EM+MI-WeM6, 25
Roychowdhury, T.R.: TF+SS-TuA10, **23**
Rubloff, G.: TF2-MoM5, **8**
Ruzic, D.N.: PS+TF-MoM1, 2; SS+EM+PS+TF-ThA9, **40**
Ryou, J.-H.: TF-MoA4, 12
Ryu, S.Y.: TF+EM+MI-WeM11, **25**
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Saeed, A.: TF+EM+MI-WeA12, 30
Saito, M.: TF+EM+MI-WeM5, **24**
Sampath, W.S.: TF-MoA5, 12
Samukawa, S.: TF+EM+MI-WeM10, 25
Sandoval, T.E.: TF1-MoM2, **6**
Sandrez, S.M.: TF+AS+EL+EM+NS+PS+SS-ThA4, 41
Sang, X.: 2D+EM+MI+NS+TF-MoM5, 1
Sangtae, K.: TF+EM+MI+PS-MoA3, 10
Schatz, G.C.: TF1-MoM1, 6
Schlosser, D.: BI+AC+AS+HC+NS+SS+TF-WeA7, 27
Schneider, J.R.: TF-TuM11, 18
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Segawa, T.: TF-ThP17, **46**
Selvamanickam, V.: TF-MoA4, 12
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Seong Keun, K.: TF+EM+MI+PS-MoA3, 10
Shah, D.S.: TF+PS-ThM10, **35**
Shahariar, H.: TF+AS+EL+EM+NS+PS+SS-ThA10, 42
Sharma, S.: TF+PS-TuA9, 20
Shayestehaminzadeh, S.: TF+EM+MI-WeM13, 26
Sheil, R.: TF2-MoM3, **7**
Shenderova, O.A.: TF+AS-TuM5, **16**
Shi, J.: TF+SS-TuA9, 23
Shiba, Y.: TF+EM+MI-WeM5, 24
Shin, K.S.: TF-ThP14, 45
Shindo, T.: PS+TF-MoM10, 4
Shinoda, K.: PS+EM+TF-ThA3, 38; PS+EM+TF-ThM3, **31**
Shirahata, N.: TF+EM+MI-WeA1, **28**
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Sibener, S.J.: SS+EM+PS+TF-ThA6, 40
Simanjuntak, F.M.: TF+EM+MI-WeM10, **25**
Singh, J.A.: TF-TuM11, 18
Sitar, Z.: TF+AS+EL+PS-ThM1, 32
Smith, S.: TF+EM+MI+PS-MoA8, 11
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Someya, T.: TF+AS+EL+EM+NS+PS+SS-ThA1, 41
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Spiegelman, J.: TF1-MoM4, 6; TF1-MoM9, 7
Sprenger, J.K.: TF+AM+EM+PS-TuM4, **14**
Sprowl, L.H.: BI+AC+AS+HC+NS+SS+TF-WeA11, 28
Stafford, L.: PS+TF-MoM3, **2**
Stair, P.C.: TF1-MoM1, 6
Stecklein, G.: 2D+EM+MI+NS+TF-MoM2, 1
Storm, D.F.: TF+EM+MI-WeM1, 24
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Sun, H.: TF+AM+EM+PS-TuM4, 14
Sun, S.: TF-MoA4, 12
Suwa, T.: TF+EM+MI-WeM5, 24
Suzuki, A.: PS+TF-MoM10, 4
Swart, H.C.: TF+AS-TuM3, **16**
Switzer, J.: EM+2D+NS+PS+RM+TF-ThA1, **37**
Szwed, M.: TF+SS-TuA2, 22
— T —
Tait, S.L.: SS+EM+PS+TF-ThA4, 40
Takahashi, M.: TF+EM+MI-WeM3, 24
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Takeuchi, T.: PS+EM+TF-ThA1, 37
Talin, A.A.: TF2-MoM5, 8
Tan, S.: PS+EM+TF-ThA4, 38
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Teplyakov, A.V.: TF1-MoM3, 6
Teramoto, A.: TF+EM+MI-WeM5, 24
Terblans, J.J.: TF+AS-TuM3, 16
Terryn, H.: SE+NS+TF-MoM1, 4; TF+SS-TuA1, 21
Tonner, R.: TF1-MoM2, 6
Torelli, M.D.: TF+AS-TuM5, 16
Torres, T.: SS+EM+PS+TF-ThA11, 40
Toyoda, N.: PS+EM+TF-ThM10, **32**
Trotochaud, L.: TF+SS-TuA1, 21
Tsai, D.S.: 2D+EM+MI+NS+TF-MoM10, 2
Tsampas, M.N.: TF-TuM13, 19
Tulodziecki, M.: TF2-MoM4, 8
Turley, R.S.: TF+AS+EL+PS-ThM5, 33; TF-ThP24, 47
Twigg, M.E.: TF+EM+MI-WeM6, 25
— U —
Uedono, A.: PS+TF-MoM10, 4
Unnikrishnan, S.: TF2-MoM4, 8
Unocic, R.R.: 2D+EM+MI+NS+TF-MoM5, 1
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Van Elshocht, S.: TF+AM+EM+PS-TuM10, 15
van Ommen, J.R.: TF+AM+EM+PS-TuM10, 15
van Straaten, G.: TF-TuM10, **18**
Vandersmissen, K.: TF+EM+MI-WeM12, 25
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Verheijen, M.A.: TF+AS+EL+EM+NS+PS+SS-ThA6, 41
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Voigt, B.: TF-MoA8, 12
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Wallas, J.M.: TF-TuM2, **17**
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Walter, J.: TF-MoA8, 12
Walter, T.N.: TF+AM+EM+PS-TuM6, **15**
Walton, S.G.: PS+TF-MoM11, 4; PS+TF-MoM6, 3; TF+EM+MI-WeM4, 24; TF-ThP22, 47; TF-ThP38, 49; TF-TuM4, 17
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Wang, S.Y.: TF+EM+MI-WeA10, 29
Wang, X.: TF-TuM1, **17**
Wang, Y.: SE+NS+TF-MoM3, 4; TF+SS-TuA8, 22
Wang, Z.: 2D+EM+MI+NS+TF-MoM10, 2; TF-ThP29, 48
Ward, M.J.: TF-ThP31, 48
Washiyama, S.: TF+AS+EL+PS-ThM1, 32
Watt, A.A.R.: TF+AS+EL+EM+NS+PS+SS-ThA11, 43
Wheeler, V.D.: PS+TF-MoM11, 4; TF+EM+MI-WeM4, **24**; TF-TuM4, 17
Wiame, H.: TF+EM+MI-WeM13, 26
Wiggins, B.: SS+EM+PS+TF-ThA6, 40
Wilke, J.: BI+AC+AS+HC+NS+SS+TF-WeA7, 27
Wimbley, T.: TF-ThP30, 48
Winter, C.H.: PS+EM+TF-ThM5, **31**
Wisman, D.L.: SS+EM+PS+TF-ThA4, 40
Wolfe, K.M.: TF-ThP24, 47
Woo Chul, L.: TF+EM+MI+PS-MoA3, **10**
Woodward, J.M.: PS+EM+TF-ThA8, 38; TF-ThP38, **49**
Wu, B.: SS+EM+PS+TF-ThA9, 40
Wu, Y.: TF+AS+EL+EM+NS+PS+SS-ThA6, 41; TF+EM+MI-WeA11, 29
Wurch, M.: 2D+EM+MI+NS+TF-MoM2, 1
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Xia, A.: SE+NS+TF-MoM4, **5**
Xiao, K.: 2D+EM+MI+NS+TF-MoM5, **1**
Xiao, Z.: TF-ThP30, 48
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Yamada, T.: TF+EM+MI-WeA10, 29
Yan, H.M.: TF+PS-ThM12, **35**; TF-MoA10, 13; TF-MoA9, 13
Yang, J.: TF+SS-TuA11, 23
Yang, W.: PS+EM+TF-ThA4, 38
Yanguas-Gil, A.: TF-ThP31, 48
Yao, Y.: TF1-MoM3, 6; TF-MoA4, 12
Yarmoff, J.A.: SS+EM+PS+TF-ThA10, 40
Yezdi, Y.: TF+EM+MI-WeM12, 25
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Yokota, T.: TF+AS+EL+EM+NS+PS+SS-ThA1, **41**
Yook, Y.G.: TF+PS-TuA12, **21**
You, D.H.: TF+PS-TuA12, 21
You, H.S.: TF+PS-TuA12, 21
Yu, X.: TF-MoA9, **13**
Yu, X.Z.: TF+PS-ThM12, 35; TF-MoA10, 13
Yuan, H.: SE+NS+TF-MoM5, 5
Yuge, K.: TF+EM+MI-WeM3, 24
Yun, J.Y.: TF-ThP40, 50
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Zaera, F.: TF1-MoM3, 6
Zafeiropoulos, G.: TF-TuM13, 19
Zaid, H.: SE+NS+TF-MoM3, 4
Zardetto, V.: TF-MoA3, 12
Zemek, J.: TF+SS-TuA7, 22
Zeng, L.: TF+PS-TuA3, 20
Zhang, F.: TF+SS-TuA12, 23
Zhang, H.: TF+EM+MI-WeA8, 29
Zhang, K.: TF+AS+EL+EM+NS+PS+SS-ThA7, **42**
Zhang, X.: TF+AM+EM+PS-TuM6, 15
Zhang, Y.: TF+PS-ThM3, 35
Zhang, Z.: TF+EM+MI+PS-MoA4, 10
Zhao, W.: 2D+EM+MI+NS+TF-MoM5, 1
Zheng, Z.S.: TF-ThP11, **45**
Zhou, W.: SS+EM+PS+TF-ThA10, 40
Zhou, Y.: 2D+EM+MI+NS+TF-MoM6, 2
Zhu, H.: SS+EM+PS+TF-ThA10, **40**
Zhu, H.P.: TF-ThP11, 45
Zorro, F.: TF2-MoM4, 8
Zyulkov, I.: TF+AM+EM+PS-TuM12, **15**